

4. ANALYTICAL CHEMISTRY

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4. ANALYTICAL CHEMISTRY

4.1 OVERVIEW

During the past 40 years, EML has developed analytical procedures for the determination of specific gases, inorganic and organic constituents, and radionuclides. The procedures in this section are subdivided into three general categories: gases, , organics, and radionuclides. All of the procedures have been written in a detailed manner to provide the user with sufficient information to obtain a quantitative result which is accurate, precise, free from chemical interference and contamination with specified detection capabilities. These procedures are presently used at EML to obtain data for ongoing and future research programs.

The procedures described in the gases subsection have been used primarily for the Laboratory's atmospheric tracer program. These procedures are highly specific for this application, with detection limits on the order of 10^{-15} .

The procedures described in the organic subsection have been applied primarily to the analysis of certain organic compounds in sediment or soil. Primary emphasis has been the determination of polyaromatic hydrocarbons (PAHs) at low concentrations for pollutant history studies conducted at EML. Separation, purification, and concentration procedures are fully described, including expected analyte recovery for these matrices and sample sizes.

The last subsection is devoted to radionuclide measurements and radiochemical procedures. The radionuclide measurement techniques are described for alpha, beta, and gamma detection types of equipment. Information about background corrections, efficiency determination, and quality control methods and limits of detection are also included. The radiochemical procedures described are designed for various environmental matrices. The sample preparation portion introduces the procedure so that representative, homogeneous, and equilibrated samples are obtained. Next, separation and purification techniques are described to obtain a radiochemically pure sample. Measurement

techniques, including limits of detection, quality control or special procedural precautions are also included.

Further information about these procedures can be obtained from the individual listed as the principal contact person.

4.2 ATMOSPHERIC TRACER TECHNOLOGY (ATT)

4.2.1 SCOPE

For over a decade EML has participated in a number of atmospheric tracer experiments designed to provide dynamic modelers with large data bases to verify, modify, or develop computer simulations of atmospheric transport and diffusion of energy-related pollutants over long distances. The tracer technology involves the release of perfluorocarbon tracers at controlled and known rates from a source(s) into the atmosphere under well-documented meteorological conditions, and measuring the tracers at very low concentrations at various distances from the release point(s).

We will present here the analytical procedure for the determination of the perfluorocarbon tracers (PFTs), perfluoromethylcyclopentane (PMCP), perfluoromethylcyclohexane (PMCH), ortho(cis)dimethylcyclohexane (OC-PDCH), perfluorodimethylcyclohexane isomer (PDCH), and perfluorotrimethylcyclohexane (PTCH). The PFTs are quantitatively determined by gas chromatography/electron capture detection.

ATT-01

**GAS CHROMATOGRAPHIC DETERMINATION OF
PERFLUOROCARBON TRACERS**

Contact Person: Raymond J. Lagomarsino

APPLICATION

This procedure is applicable to tracers adsorbed on Ambersorb adsorbent contained in stainless steel tubes in the programmable atmospheric tracer sampler (PATs) lids (described in Section 2.2.4.2).

The procedure (Dietz, 1986) involves the heating of the PATs tubes (described in Section 2.2.4.2) to 400°C by resistance heating and desorbing the PFTs and ambient air impurities (halocarbons) into the carrier gas. The compounds pass through a temperature programmed precut column (heated by resistance heating) where the high boiling point impurities are retained. The low boiling point impurities and the PFTs are partially separated by the precut column. Further decontamination of the lighter impurities is accomplished by catalytic reduction using a first stage palladium catalyst maintained at 200°C and by venting the impurities to the atmosphere by proper timing of the carrier gas switching valves. A trap containing Florisil (FL) adsorbent is opened and the partially purified PFTs are adsorbed. Subsequent rapid resistance heating of the trap to 200°C injects the PFTs into the carrier gas of the main chromatographic column system. The desorbed tracers are further purified by passage through two palladium catalyst beds maintained at 200°C, and a Nafion permeation dryer. The purpose of the dryer is to remove moisture and halogenated acids produced by the catalytic reduction. The PFTs are then chromatographically separated by the main column and detected by the electron capture sensor. Details of the pneumatics configuration are shown in Figure 1.

SPECIAL GASES

1. 5% ultra high purity (UHP) (99.999%) hydrogen in UHP (99.999%) N₂ carrier gas.
2. Compressed air to operate the valve actuators.
3. UHP (99.999%) N₂.
4. Primary calibration standards consisting of a mixture of the four tracers: perfluoromethylcyclopentane, perfluoromethylcyclohexane, ortho-(cis) perfluorodimethylcyclohexane (with isomers), and perfluorotrimethylcyclohexane.
 - a. 1.0 $\mu\text{L L}^{-1}$ of each tracer in UHP (99.999%) N₂.
 - b. 10 nL L⁻¹ of each tracer in UHP (99.999%) N₂.
 - c. 0.1 nL L⁻¹ of each tracer in UHP (99.999%) N₂.
 - d. 1.0 pL L⁻¹ of each tracer in UHP (99.999%) N₂.

SPECIAL APPARATUS

1. Gas chromatograph, modified Varian Vista 6000 or equivalent with Ni-63 electron capture detector and 1 mV recorder or data acquisition system.
 - a. Main column
15 cm x 3.2 mm: stainless steel packed with 0.1% SP-1000 on Carbopack C, 80/100 mesh.
 - b. Precut column
53 cm x 3.2 mm thin walled stainless steel tubing packed with Unibeads 2S, 80/100 mesh.
 - c. Florisil trap
11.5 cm x 1.6 mm thin walled stainless steel tubing packed with FL, 60/100 mesh.
 - d. Catalyst
1% palladium on polyethylenimine/SiO₂ (Royer Pd Catalyst), 20-40 mesh beads.
 - e. Carrier gas purifiers
activated charcoal, 13X molecular sieve and O₂ traps.

2. PATS, power control module (base).
3. Matheson Model 3800 gas regulators or equivalent.
4. Power Mate Corporation Model BPA 2086-V constant current power supply or equivalent.
5. Primeline (Soltec) two channel strip chart recorder or equivalent to monitor the PATS adsorbent tube desorption current and FL trap desorption temperature.

A. Gas chromatograph operating conditions.

Carrier gas flow	main column system - $22 \text{ cm}^3 \text{ min}^{-1}$ precut column system - $15 \text{ cm}^3 \text{ min}^{-1}$
Catalyst temperature	200°C (Injectors A and B)
Column temperature	main column - 160°C precut column - temperature programmed - 80°C to 160°C at $160^\circ \text{ min}^{-1}$
Detector temperature	200°C
Compressed air	set at 276 kPa (40 psig) to actuate switching valves
Nitrogen	set at 207 kPa (30 psig) for PATS lid Scanivalve equalization pressure

B. Gas chromatograph relay assignments.

<u>Relay No.</u>	<u>Assignment</u>
1	V1, sample valve (SV)
2	V2, precut valve (PCV) for changing the direction of the precut column (PCC) carrier gas flow.
3	V3, flow direction valve (FDV) for loading FL trap and purging catalyst B.
4	V4, FL trap valve (FTV).
5	Desorption power - High heat.
6	Desorption power - Low heat.
7	PATS tube/FL trap power routing relay.
8	Auxiliary power to precut column (PCC) for High temperature. Relay Off for Low temperature.

C. Timed relay automation programming.

Method No.	Method time (min)	Analysis integrated time (min)	Relay On	Relay Off	Aux. temp. (°C) precut column)	Remarks
1	.00	.00			85	
	.01	.01	3,7	8		V3 (FDV) On , FL Trap relay On . Auxiliary power to PCC Off .
	.02	.02	4			V4 (FTV) On (FL Trap Open)
	.05	.05	5			High heat On FL Trap
	.08	.08	6	5		Low heat On FL Trap, High heat Off
	.35	.35	4,6			V4 (FTV), (FL Trap Off), heat Off
	.40	.40		7		FL Trap relay Off
	3.00	3.00				Total run time
3	.00	3.00			80	
	.01	3.01	2			V2 (PCV) On , PCC low Forward
	.10	3.10	1,5			V1 (SV) On , High heat On
	2.00	5.00				Total run time
4	.00	5.00	8		160	Auxiliary Power to PCC On
	.60	5.60		3		V3 (FDV) Off
	.65	5.65	4			V4 (FTV) (Trap Open)
	1.50	6.50		1,5		V1 (SV) OFF , High heat Off
	4.50	9.50		4		V4 (FTV) (Trap Closed)
	4.60	9.60		2		V2 (PCV) Off (precut Column Back-Flush)
	6.20	11.20				Total run time
5	.00	11.20			145	PCC in Back-Flush , Catalyst B purge
	.60	11.80				Total run time

D. Setting the gas chromatograph.

1. Set the 5% UHP hydrogen in UHP N₂ carrier gas pressure regulator to 690 kPa (100 psig).
2. Set the main column pressure to 276 kPa (40 psig) and adjust the main column flow to 22 cm³ min⁻¹ using a calibrated flowmeter or soap bubble spirometer. Set the precut column pressure to 104 kPa (15 psig). This pressure should give carrier gas flows of 15 cm³ min⁻¹ at vents 1, 2, and 4.
3. Adjust the Nafion permeation dryer purge gas flow rate at vent 3 to ~ 30 cm³ min⁻¹.
4. Input all GC operating conditions and the timed relay program for each method as specified in Section 4.2.3.3. Method 2 is not used because it is a permanent gas chromatograph memory default method.
5. Set the constant current power supply to 14-14.25 A.

E. Determination.

1. Attach the PATS lid containing the samples to the PATS base. Plug in the lid AFM connector into the base receptacle labelled **AFM Connector**.
2. Set the base sample **Duration** rotary switches to **0013** (13.0 min) and the **Sample Quantity** (number of tubes) to **24**. This sets the switching time between tubes and the number of tubes to be sequentially analyzed. The number of tubes desired is 23; however, the analysis sequence is such that the PFTs from a sample are not injected into the main column until Method 1 of the next analysis sequence. Turn the **Power Switch** of the base to **On**.
3. Plug the constant current power supply jack into the lid receptacle labelled **Power Desorption**.
4. Attach the UHP N₂ gas line to the lid connector labelled **To Equalization** and set the tank regulator pressure at 207 kPa (30 psig). Its purpose is to equalize the pressure to

prevent the lid Scanivalve plates from separating. Pressurize the Scanivalve and manually step through each of the 23 tubes by rapidly pushing the **Valve** step switch to assure that the Scanivalve plates are properly seated. Step to tube number "00" and leave at that tube number.

5. Pull off the lid filter at the connector labelled **To SV** and attach the polyurethane tubing purge gas outlet from V1 (SV) to this connector. Attach the V1 (SV) polyurethane tubing carrier purge gas inlet line to the lid connector labelled **To PCM**. This connects the GC carrier gas lines to the lid.
6. Turn on the constant current power supply and the two-channel strip chart recorder.
7. Turn on the compressed air, set at 276 kPa (40 psig), to operate the valve actuators.
8. To start the analysis cycle, push the PATS base **Operate** switch to **Off**, bring the **Alarm** toggle switch from **Manual** to **Multi** then back to **Manual** and finally move the **Operate** toggle switch to **Run**. Tube No. 1 will advance into position, the gas chromatograph will start and run through its automated sequence consisting of four methods.

Method 1: The FDV (V3) and FTV (V4) valves are energized and the FL trap containing the PFTs from the previous sample is heated. The desorbed PFTs are injected into the main column system (Figure 2). The precut column is in the back-flush mode.

Method 3: SV (V1) and PCV (V2) are energized to place the precut column carrier gas flow into the forward position. Heat is applied to the PATS sample tube to desorb the sample (Figure 3).

Method 4: The desorbed PFTs pass through the precut column, the column is heated to 160°C at a rate of 160°C min⁻¹. V3 is placed in standby and V4 is energized to allow effluent from the precut column to flow through the FL trap where the PFTs are adsorbed (Figure 4). V1, V2, and V4 rotate to standby, forcing the precut column carrier gas path into the back-flush mode.

Method 5: The precut column temperature is lowered to 145°C with continued back-flush to elute the residual higher boiling components out of vent 1 to the atmosphere (Figure 5).

9. At the end of 13 min, the next sample tube will step into position. This sequence will continued until all 23 sample tubes have been desorbed and analyzed.
10. Record the chromatogram. A typical chromatogram of an ambient air sample containing tracers is shown in Figure 6.
11. Integrate the tracer peaks corresponding to their appropriate retention times. Apply the appropriate response factor corrections obtained from the analysis of working standards prior to the analysis of each batch of samples. Obtain the tracer volumes from the appropriate calibration curves and convert to concentrations using the sample collection volume.
12. The retention times are based upon the start of the 13-min run. The expected retention times are as follow:

Perfluoromethylcyclopentane (PMCP)	- 1.47 min
Perfluoromethylcyclohexane (PMCH)	- 2.25 min
Ortho(cis)perfluorodimethylcyclohexane (OC-PDCH)	- 3.60 min
Meta-para perfluorodimethylcyclohexane (MP-PDCH)*	- 4.17 min
Meta(cis)perfluorodimethylcyclohexane (MC-PDCH)	- 4.43 min
Para(trans)perfluorodimethylcyclohexane (PT-PDCH)	- 4.84 min
Perfluorotrimethylcyclohexane (1-PTCH)	- 9.20 min
Perfluorotrimethylcyclohexane (2-PTCH)	- 9.73 min

*Combination of the meta(trans) and para(cis) perfluorodimethylcyclohexane.

LOWER LIMIT OF DETECTION

Lower limit of detection (LLD) is defined here as that amount which gives detector response equal to three times the noise level (ACS, 1980). The LLDs are:

<u>Perfluorocarbon</u>	<u>LLD (fL)</u>
PMCP	2.7
PMCH	4.0
OC-PDCH	2.2
MP-PDCH	2.1
MC-PDCH	2.0
PT-PDCH	4.0
PTCH	3.9

DATA ACQUISITION AND REDUCTION

A. Computer hardware.

1. IBM personal computer AT with a minimum of 512 kilobytes system memory, 20 megabyte hard-disk drive, 5 1/4 inch floppy disk drive, enhanced graphics adapter card, graphics memory expansion card (64K) or equivalent.
2. IBM enhanced color display monitor offering 640 by 350 screen resolution and keyboard or an equivalent monitor and keyboard.
3. Nelson Series 760 intelligent A/D interface box or equivalent.
4. Citizen Model MSP-20 printer or equivalent.
5. Standard IEEE-488 (GPIB) cable.
6. Dysan 5 1/4 inch high-capacity, 96 TPI floppy diskettes or industry equivalent.

B. Computer software.

1. Nelson Analytical Corp. Model 2600 chromatography software package. Other software vendors provide equivalent packages.
2. Nelson Analytical Corp. Model 2660 peak summary tables software (optional).
3. Nelson Analytical Corp. Model 2670 batch reprocessing software (optional).

C. General procedure.

The electron capture detector (ECD) signal from the Vista 6000 gas chromatograph is monitored in real time by the Nelson intelligent interface offering 20 bit precision. The interface digitizes the detector signal and stores the values in its memory. When the data are available in the interface and the operating program is the 2600 software ACQUIRE on the IBM AT, the data is transmitted to the computer according to the METGEN method. The software detects peaks, determines their baselines, integrates these peaks, and then calculates the component concentrations. Three data files are created for each sample. They are distinguished by their file extensions: .PTS, .HDR, and .ATB. In the .PTS file, raw chromatographic mV data are saved in binary form, while in the .HDR file, parameters for sample identification pertaining to that raw data are stored in ASCII form. The peak heights and/or peak areas obtained from integration, as determined by the method, are stored in the .ATB file. Baselines different than those specified in the method may be drawn using the software's timed events capability. The values from the reintegration may be overwritten in the .ATB file. A schematic of the data acquisition and data reduction system is shown in Figure 7.

CALIBRATION

A. Standards preparation.

Presented here is a procedure for the preparation of PFT standards for both instrument calibration and daily working standards. The daily standards are analyzed prior to the analysis of a batch of samples to determine response factor corrections resulting from

changes in electron-capture sensitivity. This method is applicable to PATS lids (described in Section 2.2.4.2).

B. Special apparatus.

1. Matheson Model 3800 gas pressure regulator or industry equivalent.
2. Nupro Model SS-4BMG gas flow regulating valve or industry equivalent. **Caution:** Low concentrations of tracer material could be adsorbed with other type valves.
3. A complete PATS unit consisting of a base (PCM) and a baked-out lid (AFM).
4. Teledyne-Hastings-Raydist Model HBM-1A bubble spirometer or industry equivalent, NIST traceable.
5. A 1A cylinder containing 1 fL L⁻¹ each of PMCP, PMCH, OC-PDCH and PTCH in UHP N₂.

C. Sample preparation.

1. Plug the battery charger into the port labelled **Chg.Jack** and a jumper in the receptacle labelled **Analysis**. The purpose of the jumper is to disable the sampling pump. Set the thumbwheel switches to the following settings:
 - a. **Set Time/Alarm:** set to the appropriate time of day.
 - b. **Duration:** set to the time in minutes desired for each tube to remain in line position.
 - c. **Sample Quantity:** set to 24. The sample quantity (23 in this instance) must always be set for one more tube than is physically present on a lid.
 - d. **Day Select:** place to the **On** position for the appropriate day of the week.
2. Plug the lid connector into the base receptacle marked **AFM Connector** and turn the **Power Switch** of the base to the **On** position.

3. Set the Matheson purity N₂ tank pressure to 207 kPa (30 psig) and attach the 3.2 mm polyurethane tubing line from the cylinder to the equalization inlet port labelled **To Equalization** on the lid. Open the N₂ supply to pressurize the Scanivalve and manually cycle through each of the 23 tubes. This is done by a rapid push of the **Valve** step switch. Make sure that the LCD display indicates that tube "00" is in line after this is completed.
4. Attach the 3.2 mm polyurethane tubing from V2 of the standard gas flow control system (Figure 8) to the lid port labelled **To SV**.
5. Set the pressure of the standard cylinder containing the PFTs to 207 kPa (30 psig). Slowly open the regulator valve (V1) to permit tracer gases to flow into the PATS lid through the Nupro Flow Control Valve (V2).
6. Connect the 3.2 mm polyurethane tubing from the outlet of the lid labelled **To PCM** to a calibrated flowmeter and adjust V2 to obtain 50 cm³ min⁻¹.
7. Remove the calibrated flowmeter and replace with the bubble spirometer.
8. Using a stopwatch, time a soap bubble to travel from 0 to the 100 cm³ marks. Record the time and convert minutes and seconds to a pure minute time frame.
9. The quotient of 100 and the time is the flow rate of a mixed tracer gas.
10. If the flow rate is <49.0 or above 51.0 cm³ min⁻¹, fine adjust the needle valve to obtain ~ 50 cm³ min⁻¹.
11. Repeat Step 8 at least four times. The precision of the average of the four measurements should be within 2%.
12. Disconnect the tubing from the outlet of the lid to the bubble spirometer.
13. To load daily working standards, set the **Duration** to **0002** (2 min) to load 100 fL of tracers onto each tube.

14. A signal must be given to inform the PATS logic to start the time sequence that indexes the first tube into position. To start the sequence push the **Operate** toggle switch to **Off**, move the **Alarm** toggle switch from **Manual** to **Multi** to **Manual** and finally push the **Operate** switch to **Run**.
15. The first tube will switch into line and 100 cm³ of PFT gas will flow through the tube over a 2-min period. At the end of the 2-min period, the next tube will switch into position. This cycle will continue for 23 tubes. The actual volume of each PFT adsorbed on each tube is calculated by multiplying the average of the four measurements of flow rate obtained from Step 11 by time and by the value of the standard of each tracer affixed to the standard (fL).

$$\text{Volume of PFT added} = \sum_{i=1}^n f_i / n \times \text{fL standard} \times \text{time}$$

where f_i is the value of the i th flow measurement in cm³ min⁻¹.

16. After tube "00" appears on the tube LCD, push the **Operate** switch to **Off** and shut all cylinder valves.
17. Disconnect all tubing and place a 1/2 hole septum over the lid inlet and outlet ports.
18. Disconnect the lid plug from the base and remove the entire lid from the base.
19. For preparing standards up to 5 x 10⁶ fL, the same loading procedure is followed by using the appropriate standard for the desired range of tracer quantities and setting the flow rate and time. The PATS base time setting may be increased during a run so that by extending the time, increased tracer quantities may be loaded from one adsorbent tube to the next. For constructing a calibration curve, the standards are prepared in triplicate. Data (peak height or area) obtained from the analysis of the standards in the 10² to 10⁶ fL range are fitted by a 6th-order polynomial. A linear fit is applied below 100 fL.

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Subcommittee on Environmental Analytical Chemistry, American Chemical Society
(ACS), Committee on Environmental Improvement (1980)

"Guidelines for Data Acquisition and Data Quality Evaluation in Environmental
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Anal. Chem., 52, 2242-2248 (1980)

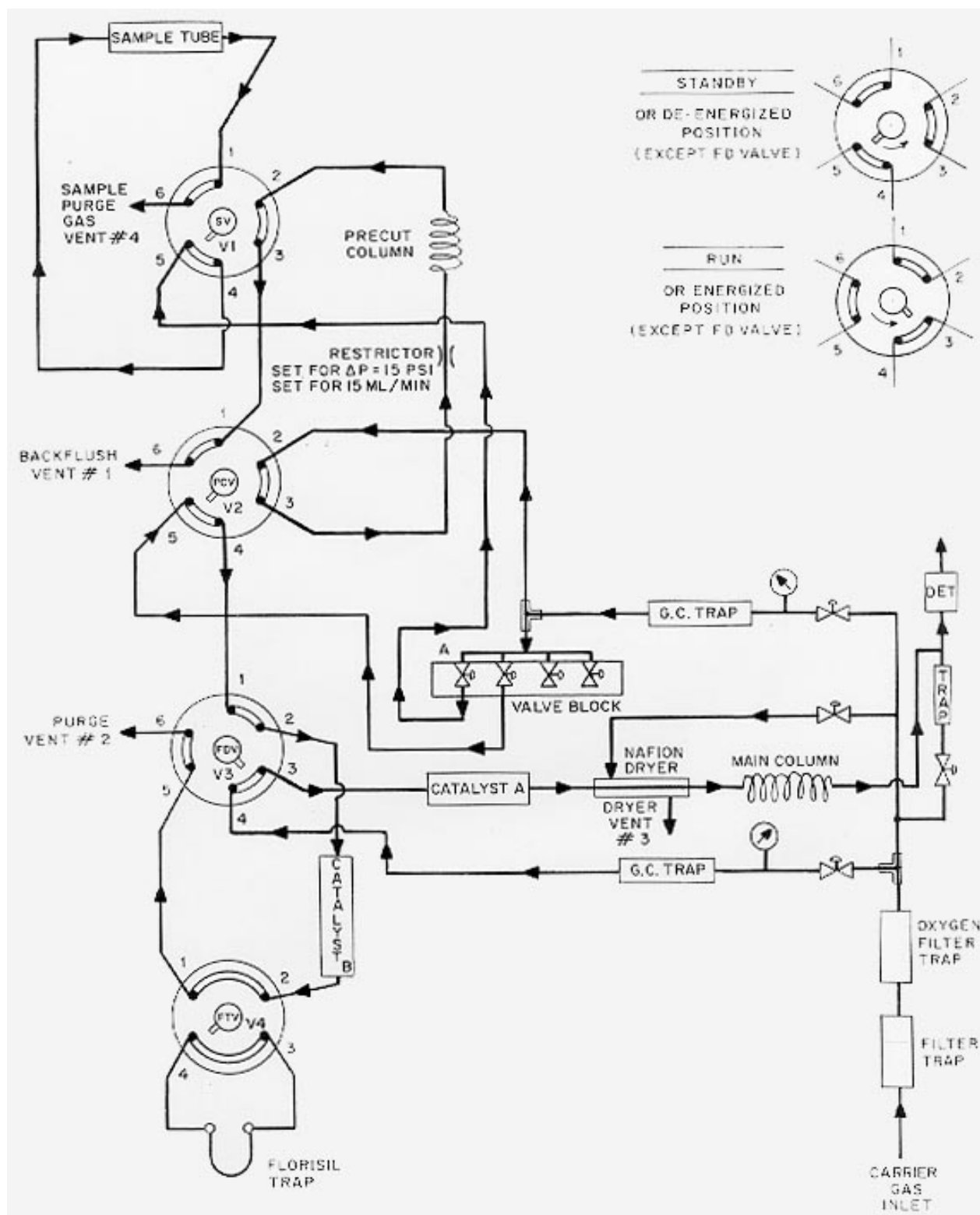


Figure 1. Pneumatics configuration of the perfluorocarbon tracer gas chromatograph.

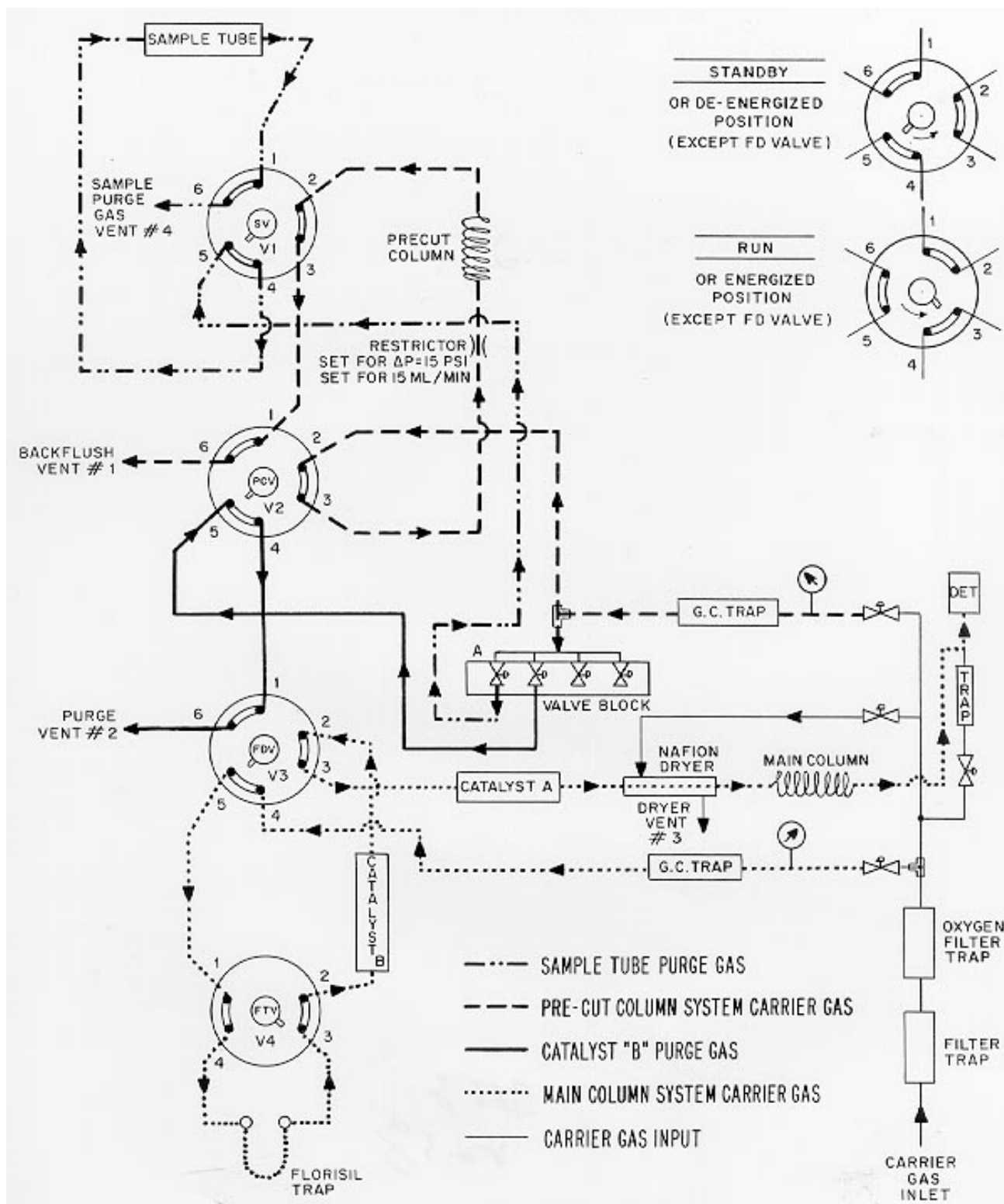


Figure 2. Method 1: carrier gas flow paths - Florisil trap desorption.

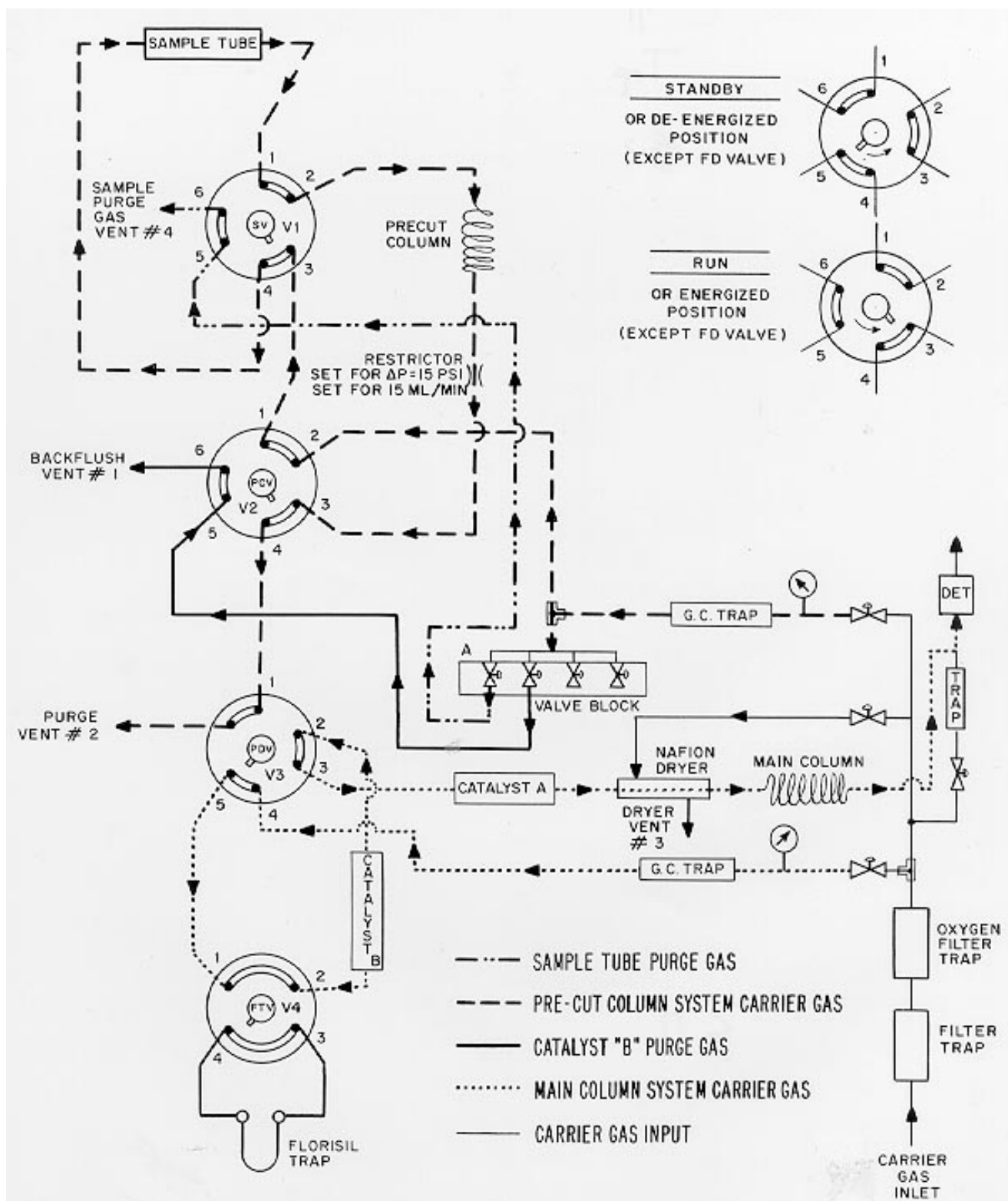


Figure 3. Method 3: carrier gas flow paths - PATS sample desorption.

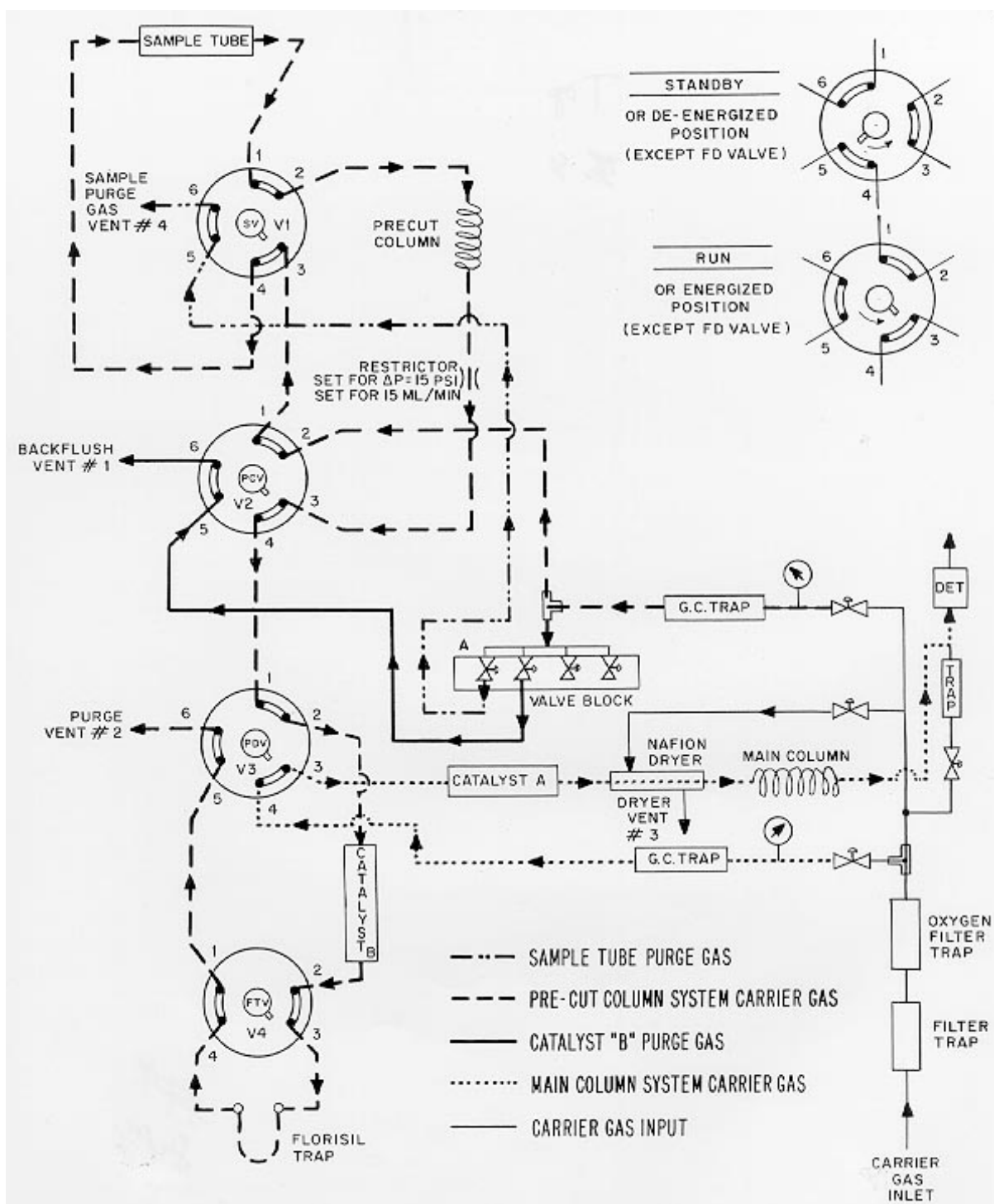


Figure 4. Method 4: carrier gas flow paths - absorption of PFTs on Florisil trap.

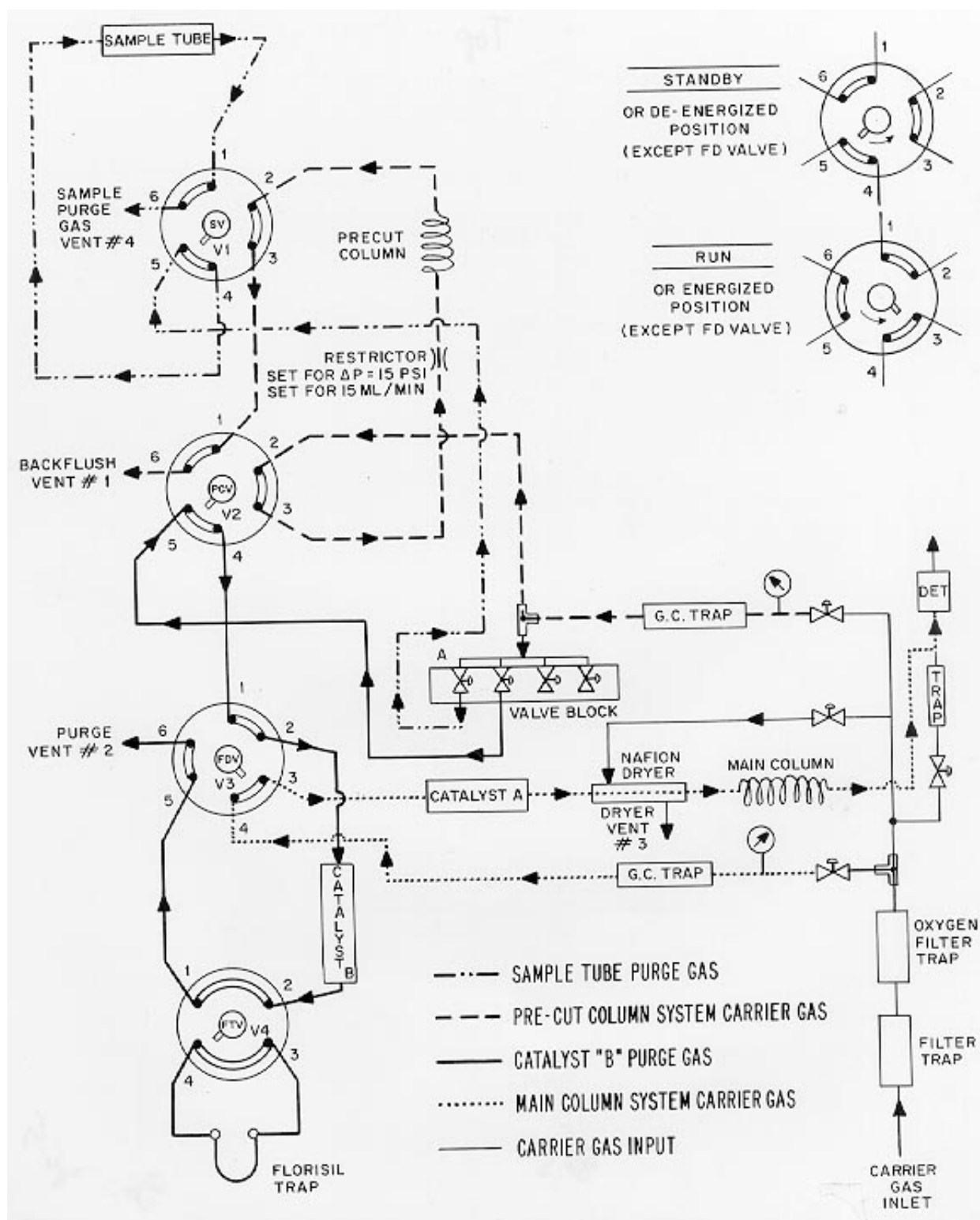


Figure 5. Method 5: carrier gas flow paths - pre-cut column back-flush..

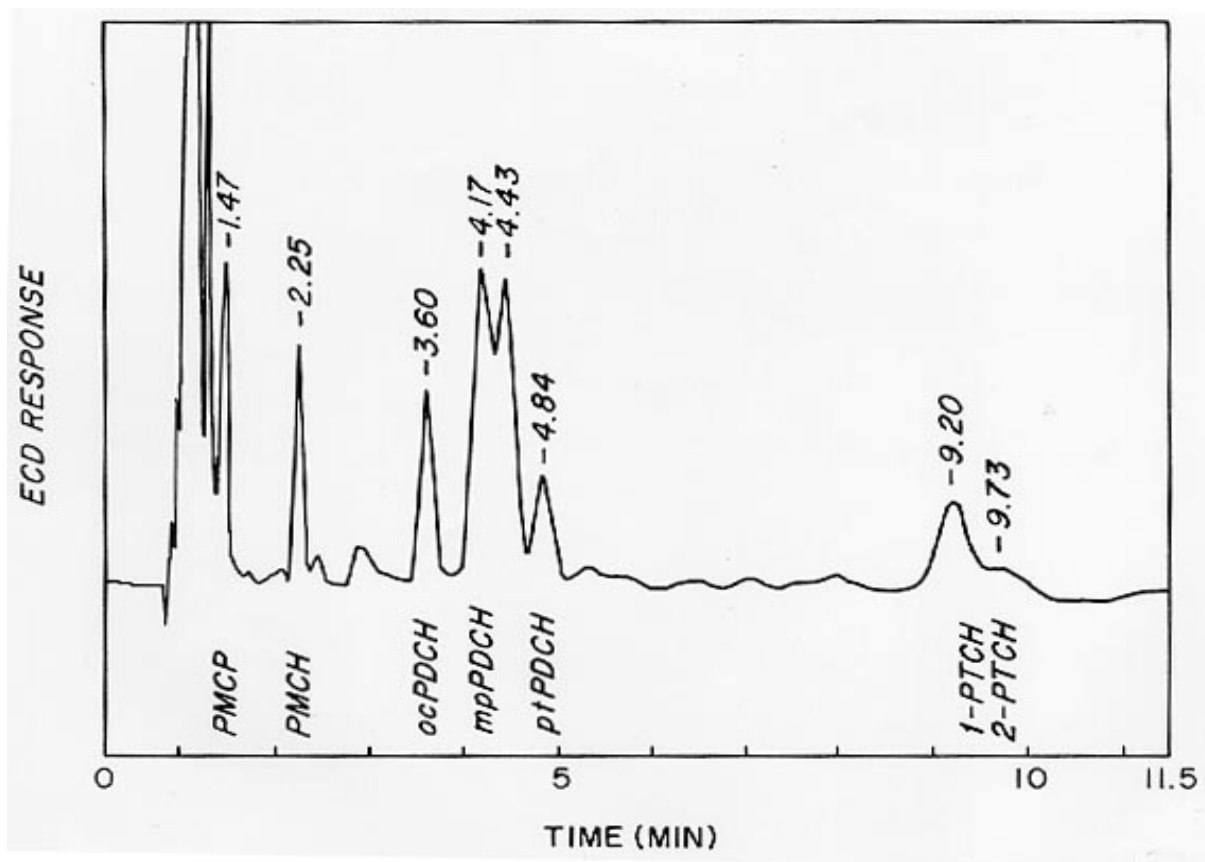


Figure 6. Chromatogram of a 72L ambient air sample containing perfluorocarbon tracers.

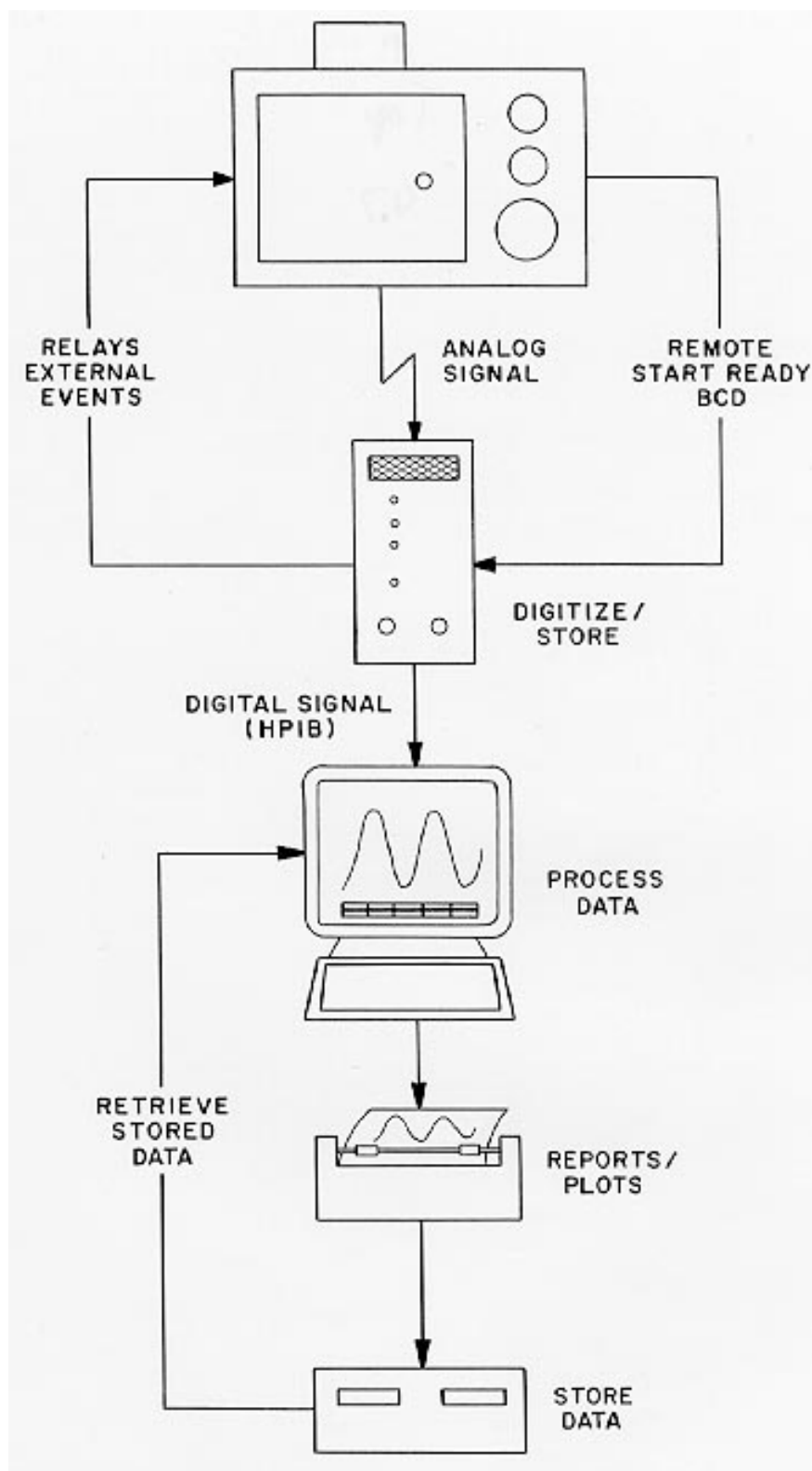


Figure 7. Schematic diagram of the data acquisition and data reduction system.

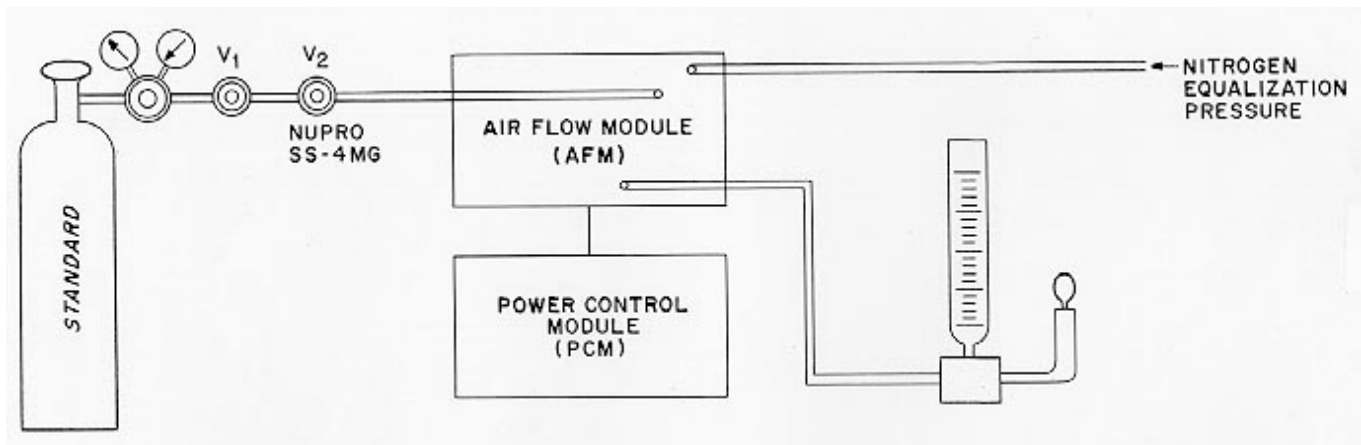


Figure 8. PFT standard sample preparation system.

4.3 INORGANICS

4.3.1 SCOPE

The inorganic procedures previously presented in this section are not currently in use and are now in Volume II. These procedures were adapted for inorganic constituent analyses in air filter extract, water, rain water, and certain soils and sediments. Atomic absorption spectrometry is used for determination of metals, ion chromatography for specific anions, and a specific ion electrode is used for fluoride determination. These procedures have been thoroughly tested; accuracy, precision, and lower limits of detection have been established. Effects from interferences and contamination are detailed in each appropriate procedure.

4.3.2 Elemental Analyses

Anions-01-E

ANIONS - ION CHROMATOGRAPHY
(see Volume II)

Ca-01-E

CALCIUM - ATOMIC ABSORPTION SPECTROMETRY

(see Volume II)

Ca-02-E

CALCIUM - PERMANGANATE TITRATION OF THE OXALATE
(see Volume II)

F-01-E

**FLUORIDE IN SOIL AND SEDIMENT - SPECIFIC
ION ELECTRODE MEASUREMENTS**
(see Volume II)

Hg-01-E

MERCURY - ATOMIC ABSORPTION SPECTROMETRY
(see Volume II)

NH₃-01-E

**AMMONIUM IN WATER AND PRECIPITATION SAMPLES -
AUTOCOLORIMETRY**
(see Volume II)

Sr-01-E

STRONTIUM - ATOMIC ABSORPTION SPECTROMETRY
(see Volume II)

U-01-E

URANIUM IN URINE - FLUORIMETRY
(see Volume II)

4.3.3 Multielemental Analyses

M-01

CADMIUM AND LEAD IN HUMAN EXCRETA AND COMPOSITE DIET SAMPLES
ATOMIC ABSORPTION SPECTROMETRY
(see Volume II)

M-02

**PRECIPITATION AND LAKE WATER SAMPLES -
PHYSICAL AND CHEMICAL MEASUREMENTS**
(see Volume II)

M-03

**TRACE METALS - ATOMIC ABSORPTION AND/OR
EMISSION SPECTROMETRY**

(see Volume II)

4.4 ORGANICS

4.4.1 SCOPE

The organic pollutants studied at EML are combustion related. Of particular interest are pollutants which are toxic, resistant to natural degradation, and that accumulate in the environment. Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) fit into this category and have been analyzed at EML in sediment samples (Tan et al., 1993).

The anthropogenic PAHs in the environment are formed primarily by pyrolysis of carbonaceous materials and the major source is the combustion of fossil fuels. Various combustion processes, especially those involving chlorinated aromatic compounds, generate PCDD/Fs. These compounds are of particular interest to DOE because, besides being combustion originated, they are quite persistent chemicals and can spread throughout the environment. Some PAH and PCDD/F isomers are highly carcinogenic. The study of these compounds in sediments is important as they can reveal the magnitude of contamination, as well as their origins and historical inputs.

OR-01

PAH AND PCDD/Fs IN SEDIMENT - GC/MS

Contact Person(s) : Yulin L. Tan

APPLICATION

This procedure can be applied to the analysis of sediment for three-ring to six-ring polycyclic aromatic hydrocarbons (PAHs) and tetra- to octa- polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs).

Many organic compounds, including PAHs and PCDD/Fs, that exist in complex compositions in sediments can be extracted into organic solvents such as methylene chloride. From the extract, the PAHs can be isolated from other organics by silica gel adsorption column chromatography and Sephadex LH-20 gel permeation column chromatography, and the PCDD/Fs can be isolated by silica gel adsorption column chromatography, acid/base wash, and alumina adsorption column chromatography. Individual PAHs and PCDD/Fs in these isolated fractions can be further separated and identified with a gas chromatograph/mass spectrometer (GC/MS) by GC retention times and mass spectra. Internal standards of labeled stable isotopes serve the purpose of quantification and quality control.

SPECIAL APPARATUS

1. Hewlett-Packard (3000-T Hanover St., Palo Alto, CA 94304) 5988 GC/MS with on-column injector.
2. HP 5890 GC/Kratos CONCEPT 1S (Barton Dock Road, Unmston, Manchester, M31 2LD UK) high resolution MS with on-column injector.

3. Labconco (8111-T Prospect, Kansas City, MO 64132) chemical carcinogen glove box.
4. Cahn Instruments, Inc. (16207-T S. Carmenita Rd., Cerritos, CA 90701), automatic electrobalance.
5. Whatman Soxhlet extraction thimbles, 33 x 80 mm, cleaned by Soxhlet extraction with CH_2Cl_2 .
6. Buchi rotary evaporator (Brinkmann, Westbury, NY 11590).
7. Fused silica capillary columns, bonded with DB-5, 30 m x 0.25 mm i.d., 0.25 μm film (J & W Scientific Inc., Folsom, CA 95630).
8. On-column syringes.
9. Amberized microflex tubes, 5 mL and 1 mL.
10. Milli-Q reagent grade water system (Millipore Corp., 80-T Ashby Rd., Bedford, MA 01730).
11. Volumetric flasks, 25 mL, 150 mL, 300 mL.
12. Narrow mouth amber glass bottles, 60 mL, with Teflon-lined screw caps.
13. Glass columns (40 cm x 19 mm i.d.), for gel permeation chromatography, with Teflon stopcocks and 250-mL reservoirs having 24/40 female joints for 24/40 stoppers.
14. Filter paper, Whatman No. 41, 2.5 cm, cleaned by Soxhlet extraction with CH_2Cl_2 .
15. Soxhlet extractors, medium size.
16. Heavy-duty explosion proof centrifuge, Model EXD (Forma Scientific, Inc., Box 649, Millcreek Rd., Marietta, OH 45750).

17. Baker Bond SPE glass Teflon columns and adapters (J. T. Baker, 222-T Red School Lane, Phillipsburg, NJ 08865).
18. 60-mL separatory funnels with Teflon stopcocks and stoppers.
19. Separatory funnel shaker.
20. Glass columns (14 cm x 5.5 mm i.d.), for alumina column chromatography, with Teflon stopcocks and 50-mL reservoirs.

SPECIAL REAGENTS

1. Distilled in glass - methylene chloride, hexane, and toluene (Burdick and Jackson, Muskegon, MI 49442).
2. PAH solutions - in the Labconco glove box, put about 100 µg each of the following standard PAHs (from various suppliers: Aldrich, P.O. Box 335, Milwaukee, WI 53201; Analabs, North Haven, CT 06473; Ultra Scientific, North Kingston, RI 02852; and Community Bureau of Reference (BCR), Brussels, Belgium) into separate 5-mL amberized microflex tubes:

phenanthrene, anthracene, 1-methylphenanthrene, fluoranthene, pyrene, 1-methylpyrene, benzo(ghi)fluoranthene, benz(a)anthracene, chrysene, triphenylene, benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene, benzo(e)pyrene, benzo(a)pyrene, perylene, indeno(1,2,3-cd)pyrene, dibenz(a,c)-anthracene, dibenz(a,h)anthracene, benzo(ghi)perylene.

Dissolve each of the PAHs into 5 mL of CH₂Cl₂.

3. SRM-1647 (priority pollutant PAHs, NIST).
4. PAH standard solution - using the Cahn 25 automatic electrobalance in the Labconco glove box, quantitatively weigh an amount of about 5 mg each of the following PAHs into a 50-mL volumetric flask:

phenanthrene, anthracene, 1-methylphenanthrene, fluoranthene, pyrene, 1-methylpyrene, benzo(ghi)fluoranthene, benzo(b)fluoranthene, benzo(a)pyrene, benzo(e)pyrene, perylene, indeno(1,2,3-cd)pyrene, dibenz(a,h)anthracene, benzo(ghi)perylene.

Dissolve the weighed PAHs with 50 mL of toluene so that the concentration of this primary standard solution contains about $100 \mu\text{g mL}^{-1}$ for each PAH. Transfer the solution to a 60-mL narrow mouth amber glass bottle with a Teflon-lined screw cap and store in a refrigerator. Mix quantitative amounts of the primary standard and SRM-1647. The mixture is analyzed as PAH calibration solutions by measuring the molecular ions of the PAHs with GC/MS according to Steps 1-8 of **Determination**, Section A. Calibrate the concentrations of each PAH in the standard solution based on the PAH concentrations in SRM-1647. Use the method of standard additions for PAHs that are present in both solutions. For PAHs present only in the standard solution, response factors of neighboring PAHs in the gas chromatogram are used.

5. Labeled PAH solution - Using the Cahn 25 automatic electrobalance in the Laconco glove box, quantitatively weigh an amount about 2 mg each of the following deuterated PAHs into a 50-mL volumetric flask:

anthracene, fluoranthene, pyrene, chrysene, benzo(e)pyrene, perylene, benzo(ghi)perylene

Dissolve the weighed deuterated PAHs in 50 mL of toluene.

6. PAH calibration solutions - Mix and dilute the labeled PAH solution and the PAH standard solution with toluene to make five calibration solutions. All five calibration solutions contain $5 \mu\text{g mL}^{-1}$ of each deuterated PAHs with various concentrations of native PAHs at $1 \mu\text{g mL}^{-1}$, $2 \mu\text{g mL}^{-1}$, $5 \mu\text{g mL}^{-1}$, $10 \mu\text{g mL}^{-1}$, and $25 \mu\text{g mL}^{-1}$.
7. Native PCDD/F stock solutions containing: 2378-TCDF, 12378-PnCDF, 123478-HxCDF, 1234678-HpCDF, OCDF, 2378-TCDD, 12378-PnCDD, 123678-HxCDD, 1234678-HpCDD, and OCDD, 1 mg mL^{-1} each in toluene.
8. PCDD/F spiking solution - mix and dilute labeled PCDD/F solutions:

$^{13}\text{C}_6$ 2378-TCDF, $^{13}\text{C}_6$ 23478-PnCDF, $^{13}\text{C}_6$ 123478-HxCDF, $^{13}\text{C}_{12}$ 1234678-HpCDF, $^{13}\text{C}_{12}$ 2378-TCDD, $^{13}\text{C}_{12}$ 12378-PnCDD, $^{13}\text{C}_{12}$ 123678-HxCDD, $^{13}\text{C}_{12}$ 1234678-HpCDD, and $^{13}\text{C}_{12}$ OCDD from Cambridge Isotope Laboratory (Woburn, MA 01810) with toluene so that the spiking solution contains 100 ng mL^{-1} each of the labeled PCDD/Fs.

9. PCDD/F calibration solutions - mix and dilute the PCDD/F spiking solution and the native PCDD/F stock solutions with toluene to make six calibration solutions. All six calibration solutions contain 10 ng mL^{-1} of each labeled PCDD/Fs in the PCDD/F spiking solution with various concentrations of each of the native PCDD/Fs listed in Step 7 at 1 ng mL^{-1} , 2 ng mL^{-1} , 5 ng mL^{-1} , 10 ng mL^{-1} , 25 ng mL^{-1} , and 50 ng mL^{-1} .
10. Sulfuric acid, ACS reagent (Fisher Scientific, 52 Faden Rd., Springfield, NJ 07081).
11. KOH solution, 20% by weight in Milli-Q water.
12. Copper powder - electrolytic purified (Fisher Scientific, 52 Faden Rd., Springfield, NJ 07081), freshly activate before use by soaking in 6N HCl for 5 min then rinsing thoroughly with Milli-Q water, followed by methanol.
13. Sephadex LH-20, Sigma Chemicals Co. (P.O. Box 14508, St. Louis, MO 63178) - swell overnight in 1:1 methanol-methylene chloride before column packing.
14. Silica gel, 100-200 mesh, EM Science (480-T Democrat Rd., Gibbstown, NJ 08027), Grade 923, cleaned by Soxhlet extraction with methylene chloride, activated at 120°C overnight, then stored in a desiccator.
15. ICN alumina B, activity 1 (ICN Pharmaceuticals, Inc., 3300-T Hyland Ave., Costa Mesa, CA 92626) cleaned by Soxhlet extraction with methylene chloride, activated at 150°C overnight, then stored in a desiccator.
16. Glass beads, 0.5 mm, cleaned by Soxhlet extraction with CH_2Cl_2 .
17. Zero gases, He, H_2 , air, and N_2 (Matheson Gas Products, 30-T Seaview Dr., P.O. Box 1587, Secaucus, NJ 07096).
18. Perfluorotributylamine, Hewlett-Packard calibration compound.

SAMPLE PREPARATION

A. Sediment handling.

1. Centrifuge the watery sediment and decant off the excess water.
2. Dry the sediment in a freeze dryer.
3. Pulverize the dried sediment in a mortar and pestle and then sieve with a No. 40 (0.425 mm) sieve to remove stones and extraneous material. The fines are collected for analyses.

B. Extraction.

1. Place the fine sediment in a cleaned Whatman extraction thimble, 33 x 80 mm.
2. Spike appropriate amounts of labeled PAH and labeled PCDD/F solutions close to those of the estimated analytes.
3. Soxhlet extract the sample with CH_2Cl_2 for 30 h.
4. Concentrate the extract to dryness with a rotary evaporator at room temperature.

C. Silica gel adsorption chromatography and sulfur removal.

1. Pack 250 mg of clean activated silica gel in an empty SPE glass Teflon column between two Teflon fritted disks. Tap gently for a tight packing and make sure the top of the column is evenly packed and closely held by the Teflon-fritted disk.
2. Pack 1000 mg of cleaned and activated silica gel in another empty SPE column as above.
3. Reactivate the two columns overnight at 120°C.
4. Prior to using, allow the columns to cool in a desiccator.

5. Place a piece of Whatman No. 41 filter paper, ca. 1 cm I.D., onto the top of the Teflon disk of the 250 mg silica gel column, add about 0.5 g of activated copper powder, place a second piece of filter paper on top of the powder.
6. Transfer the dried residue (Step B4 of **Sample Preparation**) onto the copper powder topped 250 mg silica gel column with 2 x 0.5 mL of CH_2Cl_2 . Dry the wetted column thoroughly with dry N_2 after each transfer.
7. Wet the 1000 mg column with hexane.
8. Attach sampled 250 mg column to the top of the 1000 mg column with a Teflon column adapter.
9. Wash the two-column assembly with 3 mL of hexane, and discard the wash.
10. Elute the columns with 10 mL of hexane followed by 7 mL of 60% CH_2Cl_2 in hexane into two separate 25-mL round bottom flasks for PCDD/F and PAH fractions, respectively.
11. Evaporate the PAH fraction to dryness at 35°C under reduced pressure with a rotary evaporator.

D. Acid/base wash.

1. Transfer the PCDD/F fraction in 10 mL of hexane from Step 10 of Section C, into a 60-mL separatory funnel, add 10 mL of concentrated H_2SO_4 .
2. Shake the funnel and contents with a separatory funnel shaker for 2 min.
3. Centrifuge the funnel for 30 s.
4. Drain off the lower aqueous layer.
5. Add second 10 mL of H_2SO_4 into the funnel and repeat Steps 2-4.
6. Add 10 mL of Milli-Q water, shake briefly by hand, and repeat Steps 3-4.

7. Add 10 mL of 20% KOH solution into the funnel, and repeat Steps 2-4.
8. Add second 10 mL of 20% KOH solution and repeat Steps 2-4 once and Step 6 twice.
9. Transfer the hexane layer into a 25-mL round bottom flask and concentrate to dryness with a rotary evaporator at 35°C.

E. Alumina column chromatography.

1. Place a small amount of glass wool at the bottom of the glass column for alumina column chromatography.
2. Pack 2.5 mL of activated alumina into the column and reactivate overnight at 150°C.
3. Prior to use, cool the column in a desiccator. Once cool, add a 3-mm thick layer of dry Na_2SO_4 .
4. Transfer the residue from Step 9 of Section D with 2 x 0.5 mL of hexane onto the top of the Na_2SO_4 layer. Drain the column until the meniscus reaches the sodium sulfate layer after each transfer.
5. Wash the column with 45 mL of hexane and discard the wash.
6. Elute the column with 4 mL of 60% CH_2Cl_2 in hexane.
7. Collect the eluent and concentrate to dryness on a rotary evaporator at room temperature.

F. Gel permeation chromatography.

1. Place a piece of Whatman No. 41 filter paper, 17 mm in diameter, on the fritted glass disc of the gel permeation column. Wet the filter paper with a few drops of methanol so that the paper adheres to the fritted glass disc.
2. Pour in a layer of about 1 mL of glass beads to hold the filter paper onto the fritted glass disc.

3. Fill half the column with the eluting solvent, 1:1 methanol-methylene chloride.
4. Pour in the swelled Sephadex LH-20 to form a 37-cm tall column. After the solvent is drained to the top of the gel, place a piece of Whatman No. 41 filter paper, 17 mm in diameter, on top of the column and add a 1-cm thick layer of glass beads.
5. Transfer, dropwise, the PAH fraction (Step 11 of Section C) with three to five portions of 0.5 mL each of the eluting solvent onto the column. Spread the drops evenly over the top of the column and drain off each transferring solution before adding the succeeding portions.
6. Elute with 1:1 methanol-methylene chloride and discard the first 75 mL of the eluent. Collect the following 30 mL of eluent and dry it with a rotary evaporator at room temperature.
7. Regenerate the column by washing with an additional 50 mL of eluting solvent. Keep the column in the solvent and seal the reservoir with a 24/40 stopper.

DETERMINATION

A. PAHs.

1. Set the HP5988 GC/MS parameters as follows:

<u>Parameters</u>	<u>Description</u>
GC Column	J & W Scientific, Inc., fused silica capillary column (see Special Apparatus)
Oven temperature program	from initial 60° to 150°C, at 32°C min ⁻¹ , then from 150° to 280°C at 4°C min ⁻¹ , and hold at 280°C for 30 min
Carrier gas	He, head pressure 20 psi.
Injection mode	On-column
Ionization mode	Electron impact
Emission	300 µA
Electron energy	70 eV
Ion source temperature	150°C

2. Tune the MS with a calibration compound, perfluorotributylamine.
3. Set the MS at scan mode and mass scan range at 50-500.
4. Inject 0.5 µL of each PAH solutions (Step 2 of Special Reagents).
5. Immediately start the GC oven temperature program, and acquire the data during the GC run.
6. Determine the GC retention times of each PAH from the total ion chromatograms.

7. Switch the MS to the SIM mode, set the masses of the molecular ions of labeled and native PAHs in calibration solutions (Step 6 of Special Reagents) to be acquired in their retention windows.
8. Inject 1 μL of each PAH calibration solution and acquire the ion abundances of the selected ions at the SIM mode. Repeat five times.
9. Establish the calibration curve for each native PAH by plotting the molecular ion abundance ratios of native to labeled PAHs vs. their concentration ratios in the calibration solutions. For native PAHs without labeled counterparts, data from neighboring labeled PAHs in the total ion chromatograms are used. The slopes of these curves are the response factors, F .
10. Repeat Step 3.
11. Redissolve the residue of the PAH fraction (Step 6 of Section F) into a small amount of methylene chloride and inject 1 μL of the solution into the GC/MS.
12. Repeat Step 5.
13. Identify the PAHs in the PAH fraction by their retention times and mass spectra, considering there are superimposed spectra of spiked labeled PAHs on some of the native PAHs.
14. Repeat Step 7.
15. Inject 1 μL solution of PAH fraction and repeat Step 5.
16. Calculate the molecular ion abundance ratios of native to labeled PAHs, r .
17. Determine the concentrations of native PAHs, C , from the weight of the sample, W , amount of spiked labeled PAHs, w , the ion abundance ratios and response factors, F , as:

$$C = \frac{w \cdot r \cdot F}{W}$$

B. PCDD/Fs.

1. Set the Kratos 1S CONCEPT parameters as follows:

<u>Parameters</u>	<u>Description</u>
GC column	J & W Scientific, Inc.; fused silica capillary column (see Special Apparatus)
Oven temperature program	Hold at initial 80°C for 1 min, program from 80-200°C at 30°C min ⁻¹ , then go to 280°C at 5°C min ⁻¹ and to 300°C at 15°C min ⁻¹
Carrier gas	He, head pressure 20 psi
Injection mode	On column
Ionization mode	Electron impact
Electron energy	30-40 eV
Source temperature	250°C
Trap current	500 µA
Resolution	10,000 (10% valley definition)

2. Tune the MS with a calibration compound, perfluorotributylamine.
3. Under the GC oven temperature program, acquire the mass spectra of the native PCDD/Fs in stock solution (Step 7 of **Special Reagents**) at scan mode, mass range 50-500. Establish the retention windows of PCDD/Fs with the acquired spectra and published results (Ryan et al., 1991).
4. Set the MS at the SIM mode and acquiring ions with masses M (molecular mass with all ³⁵Cl) and M+2 (molecular mass with one ³⁷Cl and the rest ³⁵Cl) for both native and labeled tetra- to penta- PCDD/Fs isomers and M+2 and M+4 (molecular mass with two ³⁷Cl and the rest ³⁵Cl) for both native and labeled hexa- to octa- PCDD/Fs isomers in their respective retention windows.

5. Inject 0.5 μL of each PCDD/F calibration solutions (Step 9 of **Special Reagents**), start the GC oven temperature program, and acquire the ion abundances of the selected ions at the SIM mode.
6. Establish the calibration curves for each native PCDD/F by plotting the ion abundance ratios of native to labeled PCDD/F vs. their concentration ratios in the calibration solutions. The slopes of these curves are response factors, F_1 .
7. Redissolve the residue of PCDD/F fraction (Step 7 of Alumina Column Chromatography) into a small amount of toluene and inject 0.5 μL of the solution into the GC/MS.
8. Repeat Steps 4.
9. Inject 0.5 μL of solution made in Step 7 and start GC/MS run as Step 5.
10. Identify the PCDD/Fs in the PCDD/F fraction by their retention times (Ryan et al., 1991) and ion abundances.
11. Calculate the ion abundance ratios of native to labeled PCDD/Fs, r_1 .
12. Determine the concentrations of native PCDD/Fs, C_1 , from the weight of the sample, W , amount of spiked labeled PCDD/Fs, w_1 , the ion abundance ratios of native to labeled PCDD/Fs, r_1 , and F_1 , as:

$$C_1 = \frac{w_1 \cdot r_1 \cdot F_1}{W}$$

LOWER LIMIT OF DETECTION

The recovery of PAHs and PCDD/Fs from the whole sample preparation is ~ 50%. The detection limit varies from 1 to 3 pg for three-ring to six-ring PAHs on the HP5988 GC/MS, and 0.2 to 0.5 pg for tetra- to octa-PCDD/Fs on the HP5890 GC/Kratos CONCEPT 1S MS.

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Estuaries, 16, 427-432 (1993)

4.5 RADIOCHEMICAL

4.5.1 SCOPE

Described in this section are the radiochemical procedures currently in use at EML. These procedures have been constantly updated for the past 40 years to reflect current separation technology and measurement techniques. The radiochemical procedures are usually written for a distinct environmental matrix since chemical interferences and contamination levels vary according to sample type.

4.5.2 Radiometrology

A-01-R

ALPHA RADIOASSAY

Contact Person(s) : Isabel M. Fisenne

CALIBRATION OF ALPHA-EMITTING RADIONUCLIDE SOLUTIONS AND SOURCES

A. Application.

The methods for primary and secondary calibrations of α -emitting solutions and sources are described for detection systems in use at EML.

B. Description of the system.

Primary calibrations of α -emitting radionuclide solutions and sources are performed at EML with a 2π windowless (internal) gas flow proportional detection system. A commercially obtained stainless steel counter with a three-position turntable and gas flow indicator (a bubbler) is capable of accepting samples up to 5.08 cm (2 in) diameter. A heavy walled cylindrically shaped active volume contains a loop anode of stainless steel wire. An EML designed and built preamplifier is connected directly to the top of the detector. The preamplifier acts as an impedance matching device for pulses from the detection volume to an electronic scaler. High voltage from a 0-5000 V regulated power supply is applied to the anode through a cable connection on the preamplifier. The signal from the anode passes through the preamplifier and a cable into an electronic scaler. The duration of the measurement interval is controlled with an electronic timer. Methane (99.99% chemically pure) is used as the counting gas.

Any source to be measured must be of a conducting material. In practice, all sources measured at EML in this system are on metal backings, usually platinum, stainless steel or aluminum.

C. Traceability to the National Institute of Standards and Technology (NIST).

Each day the detection system is used, its operating characteristics are checked with a NIST standard reference material (SRM) U_3O_8 source. After thoroughly flushing the system with the counting gas, a voltage plateau is determined with the NIST source. Generally, the plateau is 500-600 V in length at applied voltages of 2300-2900 (+). The slope of the voltage plateau is checked and should be $< 1\%$ per 100 V with methane as the counting gas. The operating voltage selected is 100 V below the upper "knee" of the plateau. The NIST source is measured for 2000 sec, sufficient for a 1 s Poisson standard deviation (SD) of the measurement of $< 0.5\%$. The background count rate is determined at the same operating potential for 2000 sec. The background count should be 4-5 counts or about $0.003 \text{ counts sec}^{-1}$ (cps). The net count rate obtained by subtracting the background count rate from the total count rate of the standard source measurement is compared with the certified NIST value. (Total count rate refers to the [sample + background] count rate.) The NIST certified value is given in terms of α particles sec^{-1} in a 2π configuration. This means that the α backscatter factor is part of the certified value and no correction needs to be made for this source characteristic. The EML value obtained must agree with the NIST certified value (within the error of the measurement) before other sources are measured.

As a further check of this procedure, when NIST α -emitting SRM sources are purchased, they are treated as unknowns and measured as described above. The value obtained at EML is then compared with the certified value.

Failure to obtain a flat or a long voltage plateau or failure to agree with the certified source value are immediate indicators of problems in the detection system which must be remedied before proceeding with additional measurements.

D. EML source preparation.

A system for the primary calibration of α -emitting solutions and sources is maintained at EML because all the nuclides required for in-house programs may not be available as NIST SRMs at any given time and it is cost effective. Both NIST SRM solutions and sources are initially expensive and the cost of recalibration by NIST is often equal to or

more than the original cost. Since all EML α -emitting solutions and sources are recalibrated at least once a year, the cost of NIST recertification would be prohibitive.

Electrodeposited sources of α -emitting radionuclides are prepared on 17 mm diameter virgin platinum discs. These sources, once calibrated, are used as standards to determine the detection efficiencies of α -scintillation counters and solid-state α -spectrometry systems. In general, the activity of these sources is 15-20 Bq (450 pCi or 1000 dpm). The procedure for obtaining a "working standard" source is to measure the NIST SRM U_3O_8 source and background as described above, obtain a voltage plateau for the source to be calibrated, and measure the source at the proper plateau voltage for 2000 sec. The net count rate of the source is converted to an activity unit using the detection efficiency of 52%. A Poisson error term is calculated and attached to the activity value.

The calibration of an α -emitting solution differs from that for electrodeposited sources only in the method of source preparation. It is the practice at EML that sources from the solution to be calibrated be prepared in triplicate. The source mounts are 24 mm diameter virgin platinum discs. The solution to be calibrated must be essentially carrier-free. The activity of the solution should be on the order of 160-1600 Bq g⁻¹. To minimize α absorption in the source, a weighed amount of a Teflon suspension is transferred to the disc from a polyethylene transfer pipette (see Specification 7.11). About 30 μ g of Teflon beads are delivered in the 0.1-g aliquot. A weighed aliquot of the solution to be calibrated is dispensed from the transfer pipette directly into the Teflon suspension bead. As a check on possible self-absorption in the dried source, aliquot weights are varied from 0.1-0.2 g in the triplication procedure. The sources are slowly dried near a heat lamp.

After the 2π proportional detection system has been checked as described above, the first source is heated in an alcohol burner flame just until the Teflon vaporizes. This drives off any residual waters of hydration which could cause self-absorption in the source. The flamed source is immediately placed in the methane atmosphere. A voltage plateau is obtained and the source is measured as described above. This procedure is repeated for the remaining sources. The activity and Poisson counting error are calculated for each source and corrected for the aliquot weight to obtain the activity g⁻¹ of solution. A Gaussian mean and SD are calculated from the triplicate source measurements. The Gaussian SD is usually < 1%.

Dilutions of the calibrated solution may then be prepared by weight for use in various EML programs.

ALPHA SCINTILLATION MEASUREMENTS

A. Application.

The procedure was developed for α measurements of air dust samples and chemical precipitates. Perhaps its largest application has been in the determination of ^{222}Rn and ^{220}Rn concentrations from air filter samples. Routine applications include the determination of the α nuclide concentrations of low-level solutions and measurement of total α activity of radiochemically separated samples and investigations of materials for commercial uses.

The advantages of the use of ZnS(Ag) on Mylar phosphor discs were enumerated by Hallden and Harley (1960) and are paraphrased here.

Samples are measured with uniform high efficiency, since the sample is in direct contact with the phosphor and photomultiplier tube (PMT).

The phosphor sees only the sample and the face of the PMT, yielding a lower background than other α -scintillation systems and proportional counters.

Samples are completely enclosed, readily handled and stored without loss of sample integrity or cross contamination.

Counter maintenance is negligible, since the system cannot be contaminated under ordinary conditions.

Samples need not be conducting as with internal gas proportional counters.

Filter samples are held flat without curling or buckling producing a uniform counting configuration.

B. Description of the detection systems.

Essentially all α scintillation detection systems use ZnS(Ag) as the phosphor. There are basically two types of α scintillation counters in use at EML for total α measurements,

those accommodating samples using ZnS(Ag) on Mylar (Hallden and Harley, 1960; see Specification 7.11), and those with the phosphor applied as a powder to the face of a PMT tube (Curran and Baker, 1948).

The EML α -scintillation counters were designed and built by EML's Instrumentation Division (now the Technical Program Services Division). The EML α -scintillation counters accommodate the 2.54 cm (1 in) diameter nylon ring and disc sample mounting system (see Specification 7.2). The sample to be measured is placed on the nylon disc. A 2.4 cm (15/16 in) diameter die-cut phosphor disc is placed against the sample, a strip of Mylar film (see Specification 7.3) is overlaid and the assembly is locked together with a nylon ring.

A spring-loaded 2.54 cm (1 in) diameter PMT is housed in a light tight, anti-magnetic shield, facing downward. The sample ring and disc assembly is placed in a space in a pullout drawer. The drawer is closed and a knob turned to the "up" position, placing the sample assembly in direct contact with the PMT. An emitter follower network is built on the base of the PMT. The high voltage supply for the PMT is an integral part of the EML Instrumentation Division's double width nuclear instruments modules (NIM) scaler-timer assembly.

It should be noted that the α -scintillation phosphor discs were and are intended for single use, that is, they and most of the samples are disposable as a unit.

C. Calibration of the instruments.

The detection efficiencies of the EML α -scintillation counters are determined by measuring electrodeposited "working standard" sources prepared at EML. The sources are traceable to the NIST through the process described in Section C, Traceability to NIST.

Measurements with single emitter sources with energies ranging from 3-6 MeV show that the detector response is independent of the energy of the α particle. Sources of ^{226}Ra and ^{228}Th in equilibrium with their short-lived progeny were measured in the 2π proportional counter and then mounted and measured in the α -scintillation detection systems. After applying the detection efficiency obtained from the "working standards", the values obtained by α -scintillation counting agreed with those of the 2π proportional

counter within the error of the measurements. This implies that the detection efficiencies of the α -scintillation counters are independent up to 9 MeV.

Background count rates are determined for the materials commonly used in EML programs. These include platinum discs and cellulose, polystyrene and glass fiber filters. To determine the "true" background count rates of the systems, so called "nylon background" measurements are performed in which the phosphor is placed in direct contact with the nylon disc. This is especially useful when assessing the performance of each new batch of phosphors. Typical background count rates for these materials are shown below.

<u>Material</u>	<u>Background Count Rate (cpm)</u>
Nylon	0.001 ± 0.001
Polystyrene filter	0.001 ± 0.001
Cellulose filter	0.002 ± 0.002
Glass fiber filter	0.100 ± 0.010
Platinum disc (17 mm dia.)	0.012 ± 0.002

The background count rates are determined for measurement intervals of 1000 min or more.

The average detection efficiency determined from measurements of a "working standard" source electrodeposited on platinum is 51%. The source is measured twice weekly for a 100-min counting interval.

Quality control charts are maintained for the background count rates and the detection efficiencies of the α -scintillation counters. The means and SDs of each type of measurement are calculated on a monthly basis.

SOLID-STATE ALPHA SPECTROMETRY

A. Application.

The solid-state α -spectrometry systems are used primarily to determine the concentrations of radionuclides in chemically separated samples. Virtually all radiochemical analyses for α -emitting radionuclides are performed with an isotopic tracer.

For the transuranic nuclide determinations, the following tracers are used at EML: ^{236}Pu , ^{242}Pu , and ^{243}Am . Tracers used in the determination of naturally-occurring radionuclides are ^{208}Po , ^{209}Po , ^{229}Th and ^{232}U .

The systems are also used to determine the radiopurity of radionuclide solutions.

B. Description of the detection systems.

The solid-state α -spectrometry systems used at EML are divided into two groups of four detectors, one group is devoted to transuranic measurements and the other to natural radionuclide measurements. Both groups have several elements in common. All components of the systems are commercially available except as noted.

Four vacuum chambers are served by a single beltless vacuum pump. The interior diameters of the vacuum chambers allow samples to be placed as far as 5 cm from the detector. The sample holder, which may be moved vertically, has been modified at EML to an open drawer-slide arrangement. The drawer is locked in place and the slide, with a 2.54 cm diameter by 2 mm deep indentation to accommodate the sample mount, is removable. The sample is placed on a mount, the mount is placed in the indentation, and the slide is then replaced in the open drawer arrangement. This sample holder arrangement eliminates problems of source to detector geometry. The two kinds of solid-state detectors in use at EML will be discussed below. Voltage to the detectors is supplied by individual regulated power supplies. Each detector has a charge sensitive preamplifier and a linear amplifier. Signals from the detectors are directed through a router into a 4096 multichannel analyzer. One analyzer serves four detectors with data collection divided into four 1024 channel segments. A hard copy of the data is obtained with a high speed printer.

All α -spectrometry data are reduced "by hand" which ensures immediate and individual review of the spectra. By this practice, difficulties with the spectrometry systems or the samples are quickly noted and remedied.

The solid-state α detectors are operated at about 10 keV per channel, covering an energy range of about 3-13 MeV. By this practice, all α emitters present in a sample can be identified from their energies. (Virtually all α emitters, both natural and artificial are within this energy range.)

Because EML is primarily involved in the measurement of low-level environmental samples, the most common measurement period by α spectrometry is 5000 min. This time unit will be used in describing some of the characteristics of the detection systems.

The solid-state detectors in use at EML for research programs are conventional 500 mm² active area silicon surface barrier detectors. The resolution of the detectors, as measured routinely with EML prepared "working standard" sources, is 40-45 keV (FWHM). The systems are calibrated with "mixed α standards" prepared by micro-precipitation with NdF₃ (Hindman, 1983; Sill, 1981) on polystyrene filters. The background count rates determined with "blank" micro-precipitates in the energy regions of interest are generally 1 to 2 counts 5000 min⁻¹. The emitter mixture of the standards is ^{238,239,242}Pu, ²⁴⁴Cm. The standard and sample measurements are performed at a distance of 1 mm from the lip of the detector housing. At this distance the average detection efficiency is 40%.

The detection efficiencies and resolution obtained with microprecipitated standards were checked against those obtained with electrodeposited standards and no differences were found.

The multichannel analyzers used for α -spectrometry measurements have been thoroughly tested by EML's Instrumentation Division to ensure stability over long measurement periods (5000-10,000 min). The stability of the systems is aided by placing them in a temperature controlled room. It is important to note that the room temperature needs to be stable. It is fluctuations in temperature that cause the detector response to shift or drift.

A commercially available hardware/computer controlled system is used for routine measurements. There are eight vacuum modules, each housing a 500 mm² ion implant detector. To accommodate the software requirements of the system, the detectors are calibrated with NdF₃ microprecipitated "working standards" containing only two emitters, ²⁴²Pu and ²⁴⁴Cm. The resolution of the detectors is about 50 keV FWHM and the detection efficiency about 40%. Background count rates are similar to our research systems.

B. Calibration of the alpha-spectrometry systems.

The detection efficiencies of the α -spectrometry systems are determined by measuring microprecipitated "working mixed standards" prepared at EML. The activity of the standards is determined by α -scintillation counting on systems calibrated with sources traceable to NIST through the process described in Section C, Traceability to NIST.

Measurements with single emitter sources with energies ranging from 3-6 MeV have shown that the energy and detection efficiency responses of silicon surface barrier detectors are constant. Sources of ²²⁸Th in equilibrium with its short-lived progeny were measured and the activities of the individual progeny were the same within the error of the measurements. This provided empirical information that the energy response of the detectors is constant up to 9 MeV and implies that the detection efficiencies are also constant.

It is the practice at EML to measure the background count rate of the detectors each weekend and during the week if the work load permits. Typical background count rates for the detectors are given above. The background count rates of the systems invariably increase with time due to recoil atoms depositing on the face of the solid-state detectors. It has been the experience at EML that the background count rates become unacceptable after two years of use. The only effective method of reducing the background count rates is to place the detectors in a high vacuum provided by a liquid nitrogen cooled diffusion pumping system over a weekend.

Each "working mixed standard" source has a total activity of about 15 Bq. The standards source is measured for 50 min before and after each sample measurement. The standard source measurements provide three important pieces of information: the

detection efficiency, the detector resolution, and the energy calibration. Deviations from normal operating conditions in any or all of these characteristics are immediately investigated. These quality control records are very important in establishing the norm for each detector system.

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BETA RADIOASSAY

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CALIBRATION OF BETA-EMITTING RADIONUCLIDE SOLUTIONS

A. Application.

The methods for the primary calibration of emitting radionuclide solutions and routine measurements are described for detection systems in use at EML.

B. Description of the system.

Primary calibrations of β -emitting radionuclide solutions are performed at EML with gas flow 4π β -proportional and 4π β -proportional- 4π γ coincidence detection systems. The commercially obtained aluminum proportional counters have a stainless steel wire anode in each half-cylinder. The total interior volume is 50 cm³. The source mount is an aluminum washer, 3.8 cm in diameter with a 1.8-cm diameter center hole and four 0.3-cm holes in the rim to allow gas to flow between the halves with the source mount in place. The counting gas is 99.99% chemically pure methane, and the flow through the chamber is monitored with a bubbler. An EML designed and built emitter follower preamplifier is connected directly to the anodes. Signals from each half of the chamber are summed prior to further amplification. The amplifier is arranged to deliver triggered pulses to an electronic scaler. High voltage is supplied by a 0-5000 V regulated power supply. The chambers exhibit rather long (600 V) and flat (<0.5% per 100 V) counting plateau. The 4π β detection system is unshielded and has a background rate of 0.7 counts sec⁻¹ at 3500 V, the usual operating voltage.

In the $4\pi\beta$ - $4\pi\gamma$ -coincidence detection system, the chamber is mounted between two 7.6 x 12.7 cm NaI(Tl) crystals. The entire detection assembly is lead shielded. The upper crystal is pneumatically raised and lowered to permit access to the chamber. The signals from the two crystals are summed, amplified, and processed through a single channel analyzer, and simultaneously recorded into a scaler and a multichannel analyzer. High voltage to the crystals is supplied by a single 0-1500 V regulated power supply. As described above, the signals from the chamber are summed and amplified, but then split into the variable coincidence gate and a scaler. The output signals from the variable coincidence gate unit are fed into a third scaler. The three scalers are controlled by a master timer.

A detailed discussion of the $4\pi\beta$ - γ -coincidence method can be found in the National Council on Radiation Protection and Measurements Report No. 58 (NCRP, 1985).

C. Traceability to the National Institute of Standards and Technology (NIST).

Traceability to NIST is difficult since suitable standard reference material (SRM) sources are not available for many radionuclides. Our approach over the years has simply been to recalibrate NIST SRM solutions or solutions obtained from commercial vendors who are traceable to NIST using EML source preparation techniques and detection systems. Except for discrepancies caused by differences in the use of decay scheme parameters, the EML results are in agreement with the certified values within the error of the measurements.

D. EML source preparation.

Two kinds of supporting films for the source mounts are used in the proportional counters, which are described below.

The first type of film support is prepared from clear vinyl paint* and is used with pure beta emitters with a maximum energy >0.25 MeV. It has been established experimentally, using NIST and commercial vendor certified standard solutions of ^{45}Ca , that the detection efficiency of this emitter is 100% for the source mounts described below.

* Flat Vinyl Ink 3900-99-Clear, obtained from: Colonial Printing Ink Co., 180-T East Union Ave., East Rutherford, NJ 07073

About 0.1 mL of paint is dropped onto a 1-cm deep layer of clean cold water in a 50 cm x 75 cm tray, painted matte black on the interior surfaces. The paint spreads across the surface of the water and the film thickness is estimated visually, by color. A clear or light gray film is $\sim 5 \mu\text{g cm}^{-2}$, white is $10 \mu\text{g cm}^{-2}$, and yellow is $20 \mu\text{g cm}^{-2}$, which has been determined experimentally. At EML, the $10 \mu\text{g cm}^{-2}$ films are used as they provide the necessary strength, while still remaining extremely thin. The film is lifted from the surface of the water with a wire loop and placed over the aluminum washer. This thin film planchette is dried and then given a thin gold coating of about $10 \mu\text{g cm}^{-2}$ on one side by vacuum evaporation in a small sputterer unit. Self-absorption in the source mount is minimized using a technique developed at EML (Hallden and Fisenne, 1963). A 0.1-g aliquot of a Teflon bead suspension in water* ($100 \mu\text{g}$ of Teflon g^{-1}) is placed onto the nonconducting side of the film. The radioactive solution to be standardized is delivered by weight from a polyethylene transfer pipette, into the Teflon bead suspension on the film. In general, a 0.1-g weight of the radionuclide solution is used in the preparation of a source. The source is air dried and then gold coated to produce an entirely conducting mount.

The second kind of source mount is a 2- μm thick film of polycarbonate** that is glued to the aluminum washer. These mounts are used for measurements by $4\pi\beta$ - $4\pi\gamma$ -coincidence counting, which will correct for the absorption within the film. The remainder of the source preparation procedure is the same as described for $4\pi\beta$ measurements. (Note: The thin vinyl films will only tolerate an HCl solution of $<1\text{N}$. The stronger polycarbonate will withstand HCl concentrations of up to 6N . In addition, the polycarbonate source mounts can be dried gently under a heat lamp.) The graph below shows the $4\pi\beta$ counter detection efficiency versus β - or β^+ endpoint energies for sources mounted on polycarbonate films.

The primary radionuclide solution should be essentially carrier-free. The primary radionuclide solution to be calibrated is diluted to a concentration on the order of 1700 Bq g^{-1} . The calibration is performed with triplicate source measurements. The voltage plateau for each source is determined in order to select the proper counting

* Vanflex Teflon Emulsifier #30; obtained from: Interchem Corp., 120 Route 17N, Suite 115-T, Paramus, NJ 07652

** KIMFOIL; obtained from: Kimberly-Clark Corp., Schweitzer Division, Lee, MA 01238

voltage. The activity and Poisson counting error are calculated for each source and corrected for the aliquot weight to obtain the activity g^{-1} . Other corrections appropriate to the particular radionuclide decay scheme are made from the $4\pi\beta\text{-}\gamma$ -coincidence measurements. A Gaussian mean and SD are calculated for the triplicate sources.

Appropriate dilutions of the calibrated solution are prepared for distribution within EML for various programs.

LOW BACKGROUND GAS-FLOW PROPORTIONAL COUNTING SYSTEM

A. Application.

The only routine beta analysis conducted at EML is the determination of ^{90}Sr by measurement of ^{90}Y . These measurements are performed in the LB4100TM (Oxford Instruments Inc., Nuclear Measurements Group, 601 Oak Ridge Turnpike, Oak Ridge, TN 37831-2560) low background counting system. This system is also utilized for gross alpha/gross beta determination in water and air filter samples.

B. Description of the detection system.

The LB4100 is a four drawer, 16 detector, low background counting system that is intended for gross counting of α , β and low energy x-ray emitters. The detectors are of the gas-flow proportional type. The detector slide accepts samples prepared in solid form on disks either 2.54 cm or 5 cm in diameter. Two drawers (of four detectors each) are equipped with 5 cm detectors, which are used for gross alpha/gross beta determinations. The other two drawers are equipped with 2.54 cm detectors that are used for counting the ^{90}Y samples. The detectors are mounted on a 2.54 cm Whatman No. 42 filter paper and are covered with Mylar fastened with a ring and disc assembly.

Each sample detector is the signal source for a counting channel. Each detector activates a counting channel independently of the others. Each channel has its own time control. The channels are individually deadtime corrected. The interface between the counter and the user is a computer and its keyboard.

C. Calibration of the detection system for ^{90}Y determinations.

The detectors are checked for energy plateaus and source (^{90}Sr) efficiencies prior to use or when the gas tank is changed. The background is also measured prior to use with yttrium oxalate blanks. If the instrument is idle for an extended period of time, crosstalk and yttrium oxalate efficiencies are checked. The counters are standardized with ^{90}Y oxalate with detection efficiencies of $\sim 40\%$.

LIQUID SCINTILLATION MEASUREMENTS

A. Application

The conventional liquid scintillation (LS) counting systems used at EML are designed to detect and measure low-energy (e.g., ^3H , ^{14}C) to high-energy beta particles (i.e., ^{90}Y , ^{106}Rh), and alpha particles. Samples containing mixtures of radionuclides that emit either alpha, beta, or conversion electrons are detected and quantified using variations of the LS counting technique. Depending on the LS cocktail, the alpha detection efficiency is generally $> 95\%$, whereas the beta detection efficiency is dependent on energy, spectral shape and cocktail. Typically, beta particles with maximum energies > 0.250 MeV are detected with $> 90\%$ counting efficiency.

One variation of the LS counting technique used at EML is Cerenkov counting (Scarpitta and Fisenne, 1996), which is an adjunct to LS counting that does not require a LS cocktail. Cerenkov counting in aqueous samples is applicable to beta particles with endpoint energies in excess of 0.263 MeV. The Cerenkov counting efficiency (CCE) is typically 30% per MeV for beta particles with endpoint energies above the Cerenkov threshold; alpha particles are not detected.

Another variation of the LS technique utilized at EML is photon-electron rejecting alpha liquid scintillation spectrometry (PERALS), which is designed specifically for low-level liquid scintillation alpha detection where beta/gamma interferences are eliminated and a high degree of sensitivity is desired.

The three counting methods described above require a clear liquid sample that can be counted in a short period of time (1 to 2 h). Presented in the following sections are descriptions of these methods.

B. Description of the detection system

EML's Packard Tri-Carb-2250CA LS instrument is a multitasker unit for quantitative detection of alpha, beta, positron, and conversion electron radiation. The system may be preprogrammed to select any of the 15 unique programs stored on the computer disk. The instrument can be operated in one of four counting modes: 1) conventional LS, 2) dual-DPM, 3) full spectrum analysis, or 4) efficiency tracing. The system provides computer controlled data reduction of counting results after each sample or after every batch of samples identified by the user.

The scintillation detector well is located underneath the sample changer. Samples are automatically lowered into the detector well. The detector assembly consists of two facing bi-alkali high performance photomultiplier tubes, each coupled to an optical chamber. The shielding assembly consists of a light-tight detection chamber, magnetic shielding and 5 cm of lead to reduce the effect of external radiation.

Spectrum analysis forms the basis of the Packard LS system. Typically, a beta particle will take a few nanoseconds to dissipate all of its energy in the scintillation solution. This results in an analog pulse rising to its maximum amplitude and falling to zero. The amplitude of the analog pulse is converted to a digital value. The conversion is achieved in a high speed analog to digital converter (ADC), and the digital value, which represents the beta particle energy, is the memory slot of a 0-2000 keV spectrum analyzer. The conversion by the ADC is linear so that during the measurement of a sample, the spectrum analyzer will accumulate counts representing the complete energy spectrum of the radionuclide. The spectrum analyzer is calibrated in units of keV, and the user can select one of three regions of interest over a range of 0-2000 keV.

Quenching, in general terms, refers to interferences with any of the steps of energy transferred from the solvent (where most of the energy from the ionizing radiation is initially deposited) to the scintillant and subsequent light transmission to the PMT. When a sample is quenched, the spectrum usually is shifted toward the lower energy regions, resulting in an increase in counts (i.e., apparent increase in counting efficiency) in any low

energy preset regions of interests. In most cases, a correction for this effect may be performed.

A quench-efficiency curve must be established for a given nuclide and scintillator cocktail if the sample differs in chemical composition from the reference standard used to calibrate the instrument. A series of quenched samples, containing a known constant activity for the nuclide of interest, are prepared with a measured volume of scintillation cocktail. Successively increasing amounts of a chemical quenching agent are added to the samples. The samples are then measured for spectrum analysis. A description of the quench corrections and dual-dpm analysis can be found in Scarpitta and Fisenne, (1996).

C. Calibration of the system.

The LS stability and operational acceptance criteria are checked first before running any standards or samples. This is accomplished by counting the background, and a ^3H and ^{14}C standard provided by the instrument manufacturer using an appropriate spreadsheet program. The count rate is then compared with the quality control charts developed at EML for this instrument. Descriptions of the cocktail selection, determination of window settings, and detection efficiencies can be found in Scarpitta and Fisenne (1996).

D. Cerenkov Counting

Cerenkov radiation occurs when charged particles pass through a dielectric medium (liquid) where there is an exchange of energy from the charged particle to the molecules of the medium (Haberer, 1966). The exchange energy produces local electronic polarizations in the medium if the charged particle is moving at velocities comparable to the velocity of light in the medium. When these polarized molecules return to their normal state, the excess energy is released as electromagnetic radiation known as Cerenkov radiation.

A threshold energy exists for the production of Cerenkov radiation and it is a function of the refractive index, n , of the medium. For water ($n = 1.33$) the lower energy limit of electrons for the production of Cerenkov radiation is 0.263 MeV (Berger and King, 1985). With beta emitters, the maximum energy, E_{max} , has to substantially exceed this value because of the broad beta energy spectrum. Photoelectrons and Compton electrons

from gamma emitting nuclides, having energies in excess of the threshold energy, can also be measured by Cerenkov counting. Some nuclides which can be measured by Cerenkov counting are ^{32}P , ^{35}S , ^{36}Cl , ^{40}K , ^{59}Fe , ^{89}Sr , $^{90}\text{Sr/Y}$, $^{106}\text{Rh(Ru)}$, ^{137}Cs , $^{210}\text{Pb/Bi}$, $^{234\text{m}}\text{Pa}$ (progeny of ^{238}U via ^{234}Th), and ^{99}Tc .

Cerenkov counting is an adjunct to LS analysis that does not require a scintillating cocktail. Various wavelength shifters (Haberer, 1966; Karamanos et al., 1975) have been used to enhance the CCE by 10-20% using commercially available LS spectrometers. Wave shifters are organic substances that shift the Cerenkov photon energies from a region of low detector sensitivity to a region of high detector sensitivity.

Standardized solutions, containing the equivalent of about 17 Bq (1000 dpm), are dispensed gravimetrically, in triplicate, into either 20 mL plastic or low borosilicate glass vials. Each vial was counted for 15-30 min with window settings of 0-50 keV for Cerenkov counting so that the 1 sigma counting error is <2%.

For Cerenkov counting, water is typically used as the solvent. The average instrument background, using 20-mL plastic vials containing 3-18 mL of ultra-pure water is 0.225 ± 0.018 counts sec^{-1} (cps) for a 0-50 keV region of interest. The average background count rate for glass vials (0.346 ± 0.010 cps) is about 30% higher than that obtained using plastic vials. Based on replicate background measurements, the lower limit of detection for a 1 h count at the 95% confidence level, using water as a solvent, is 0.024 cps (1.44 cpm) and 0.028 cps (1.70 cpm) for plastic and glass vials, respectively. For specific alpha/beta applications, see Scarpitta and Fisenne (1996).

E. PERALS Spectrometry

EML's PERALS spectrometer (Ordela, Inc., 1009 Alvin Weinberg Drive, Oak Ridge, TN 37830) which is a single sample stand-alone Nim Bin type unit. The unit is interfaced to a personal computer which is capable of functioning as a multichannel analyzer. The PERALS technique employs a LS detector with a pulse-shape discriminator for beta-gamma rejection (>98%) and direct extraction of the alpha activity of interest into 2 mL of a water insoluble organic phase containing the scintillator. The discriminator takes advantage of the longer decay time of light produced by alpha particle interactions to select the alpha pulses for spectrometry and reject those from beta-particle or gamma-ray events.

The choice of commercially available extractants (ETRAC Corporation) and chemical composition of the aqueous phase allows for selectivity and flexibility in sample preparation (McDowell and McDowell, 1994). The degree of beta/gamma rejection allows an instrument background (with a blank scintillator in the detector) of 0.001 cpm or less over the entire alpha energy range (3-5 MeV). The advantages of the PERALS method are that it: 1) is extremely sensitive, 2) has a high alpha counting efficiency (100%), 3) requires a count time of 1-4 h per sample or less depending on the sample activity, and 4) generates a very small amount of organic waste (<2 mL per sample).

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GAMMA RADIOASSAY

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APPLICATION

This procedure is used for the nondestructive measurement of γ -ray emitting radionuclides from a variety of environmental matrices by high resolution germanium (Ge) detector γ -ray spectrometry and NaI(Tl) detector γ -ray spectrometry. It is applicable to nuclides emitting γ -ray with energies > 20 keV for Ge detectors and 50 keV for NaI(Tl) detectors. For typical counting systems and sample types, activity levels of about 40 Bq are easily measured and sensitivities as low as .002 Bq can be achieved for many nuclides. Count rates in excess of 2000 counts sec^{-1} (cps) should be avoided because of electronic limitations. High count rate samples can be accommodated by dilution or by increasing the sample to detector distance.

The procedure is used for either qualitative, quantitative or relative determinations. In tracer work, the results may be expressed by comparison with an initial concentration of a given nuclide which is taken as 100%. For radioassay, the results may be expressed in terms of known standards for the radionuclides known to be present. In addition to the quantitative measurement of γ -ray radioactivity, γ -ray spectrometry can be used for the identification of specific emitters in a mixture of radionuclides. General information on radioactivity and the measurement of radiation has been published. Information on the specific application of γ -ray spectrometry is also available in the literature.

DESCRIPTION OF THE SYSTEM

Gamma-ray spectra are measured at EML with modular equipment consisting of a detector, an amplifier, a pulse-height analyzer, memory, and a permanent data storage device. Lithium-drifted germanium, Ge(Li), or high purity Ge detectors (p-type or n-type) are used for the analysis of complex γ -ray spectra because of their excellent energy resolutions. These Ge detectors, however, are characterized by high cost and require cooling with liquid nitrogen. Thallium activated sodium-iodide crystals, NaI(Tl), can be operated at ambient temperatures and are often used at EML as γ -ray detectors in spectrometer systems. However, their energy resolutions limit their use to the analysis of single nuclides or simple mixtures of a few nuclides.

Upon completion of the γ -ray assay, the spectral data are interpreted and reduced to nuclide activities in Bq (disintegrations per second) or related units suited to the particular application. At this time, the spectral data may be inspected on the CRT to identify the γ -ray emitters present. This is accomplished by reading the channel number from the x-axis and converting to γ -ray energy by multiplying by the appropriate keV/channel (system gain). If the system is calibrated for 1 keV per channel with channel zero representing 0 keV, the energy will be equal to the channel number. The channel number or γ -ray energy in keV is usually displayed on the CRT. Identification of nuclides is aided by catalogs of γ -ray spectra and other nuclear data tabulations. Because of the reduced spectral resolution obtained with NaI(Tl) detectors, this technique can only be applied to samples of single nuclides or very simple combinations of nuclides.

Data reduction of spectra taken with Ge spectrometry systems is usually accomplished by integration of the photopeaks above a definable background (or baseline), and by subsequent activity calculations using a library that includes data such as nuclide name, half-life, γ -ray energies and associated abundance (intensity or branching ratios). Computer programs for data reduction of NaI(Tl) detector data have been used extensively at EML. Data reduction of spectra involving mixtures of nuclides is usually accomplished by least-square fitting routines to a library of standard spectra of the individual nuclides acquired under individual conditions.

Variation of the physical geometry of the sample and its relationship with the detector will produce both qualitative and quantitative variations in the γ -ray spectrum. To

adequately account for these geometry effects, calibrations are designed to duplicate all sample counting conditions including source-to-detector distance, sample shape and size.

Electronic problems, such as erroneous deadtime correction, loss of resolution, and random summing, may be avoided by keeping the gross count rate below 2000 cps and also by keeping the deadtime of the analyzer below 5%. Total counting time is governed by the radioactivity of the sample, the detector-to-source distance, and the acceptable Poisson counting uncertainty.

In complex mixtures of γ -ray emitters, the degree of interference of one nuclide in the determination of another is governed by several factors. If the γ -ray emission rates from different radionuclides are similar, interference will occur when the photopeaks are not completely resolved and overlap. If the nuclides are present in the mixture at markedly different levels of activity, nuclides of higher energies that are predominant can cause serious interferences with the interpretation of minor, less energetic, γ -ray photopeaks. The complexity of the analysis method is due to the resolution of these interferences and, thus, one of the main reasons for computerized systems.

Cascade summing may occur when nuclides that decay by a γ -ray cascade are analyzed. Cobalt-60 is an example; 1172 and 1333 keV γ -ray from the same decay may enter the detector to produce a sum peak at 2505 keV or a count in the continuum between the individual peaks and the sum peak; thus, causing the loss of counts from one or both of the other two peaks. Cascade summing may be reduced by increasing the source-to-detector distance. Summing is more significant if a well-type detector is used.

Random summing is a function of counting rate and occurs in all measurements. The random summing rate is proportional to the total count squared and the resolving time of the detection system. For most systems, random summing losses can be held to < 1% by limiting the total counting rate to 1000 cps.

The density of the sample is another factor that can affect quantitative results. Errors from this source can be avoided by preparing the standards for calibration in solutions or other matrices with a density comparable to the sample being analyzed. Another approach is to apply attenuation corrections to all calibration standards and samples based on sample weight, known volume, γ -ray path length and average atomic number of the sample matrix.

APPARATUS

A γ -ray spectrometer consists of the following components:

A. Detector assembly.

1. Germanium detector - The detector should have a volume of at least 50 cm^3 , with a full width at one half the peak maximum (FWHM) $< 2.2 \text{ keV}$ at 1332 keV , certified by the manufacturer. A charge-sensitive preamplifier using low noise field effect transistors should be an integral part of the detector assembly. A convenient support should be provided for samples of the desired form. Vertical systems allow the standard/sample to be placed directly on the detector end cap.
2. NaI(Tl) detector - The sodium iodide crystal, activated with about 0.1% thallium iodide, should contain $< 5 \mu\text{g g}^{-1}$ of K and should be free of other radioactive materials. The crystal should be attached and optically coupled to a multiplier phototube. (The multiplier phototube requires a preamplifier or a cathode follower compatible preamplifier with the amplifier.) The resolution (FWHM) of the assembly for the photopeak of ^{137}Cs should be $< 7\%$ for a 75-mm by 75-mm detector.
3. Shield - The detector assembly should be surrounded by an external radiation shield made of massive metal, equivalent to 102 mm of Pb in γ -ray attenuation capability. It is desirable that the inner walls of the shield be at least 127 mm in distance from the detector surfaces to reduce backscatter. If the shield is made of Pb or a Pb liner, the shield must have a graded inner shield of 1.6 mm of Cd or tin lined with 0.4 mm of copper, to attenuate the 88 keV Pb γ -rays. The shield must also have a door or port for inserting and removing samples.
4. High-voltage power/bias supply - The bias supply required for Ge detectors usually provides a voltage up to 5000 V and 1 to 100 μA . NaI(Tl) detectors require a high-voltage power supply of a range of usually from 500 to 3000 V and up to 10 mA to operate the multiplier phototube. The power supply should be regulated to 0.1% with a ripple of not more than 0.01%. Line noise caused by other equipment should be removed with filters and additional regulators.

5. Amplifier - A spectroscopy amplifier compatible with the preamplifier and with the pulse-height analyzer should be used.

B. Data acquisition and storage equipment.

1. Data acquisition - A multichannel pulse-height analyzer (MCA) or stand-alone analog-to-digital converter (ADC) under software control of a separate computer, performs many functions that are required for γ -ray spectrometry. An MCA or computer collects the data, provides a visual display, and outputs final results or raw data for later analysis. The four major components of an MCA are the ADC, the memory, control, and input/output. The ADC digitizes the analog pulses from the detector amplifier. The magnitude of these pulses is proportional to the energy of the photon deposited in the detector. The digital result is used by the MCA to select a memory location (channel number) which is used to store the number of events which have occurred with that energy. Simple data analysis and control of the MCA is accomplished with microprocessors. These processors control the input/output, channel summing over set regions of interest, and system energy calibration, etc.
2. Data storage - Because of the use of microprocessors, modern MCAs provide a wide range of input and output (I/O) capabilities. Typically, these capabilities include the ability to transfer any section of data to one or more of the following: terminal, line printer, cassette tape, floppy or hard disk, X-Y plotter, and to computer interfaces via a serial or parallel port.

SAMPLE/STANDARD CONTAINERS

Sample mounts and containers must have a convenient reproducible geometry. Considerations include commercial availability, ease of use and disposal, and the containment of radioactivity for protection of the personnel and working environment from contamination. The evaporation of liquid samples to dryness is not necessary and liquid samples up to 1 L may be used. Massive samples may cause significant self-absorption of low energy γ -rays and may degrade the higher energy γ -rays. A β absorber consisting of about 6 mm of Al, Be, or plastic may be used for samples that have a significant β activity and high β energies.

CALIBRATION AND STANDARDIZATION

This section describes the analysis of mixtures of radionuclides with Ge detectors or single or simple mixtures of radionuclides with NaI(Tl) detectors. If complex mixtures of radionuclides are to be analyzed with NaI(Tl) detectors, refer to page 2 of this procedure.

A. Preparation of apparatus.

Follow the manufacturer's instructions, limitations, and cautions for the setup and the preliminary testing of all of the spectrometry equipment to be used in the analysis. This equipment would include, as applicable: detector, power supplies, preamplifiers, amplifiers, multichannel analyzers, and computing systems.

Place an appropriate volume of a standard or a mixed standard of radionuclides in a sealed container and place the container at a desirable and reproducible source-to-detector distance. For environmental analysis, most standards/samples are counted at the detector end cap. The standard should provide about 100 cps in the peaks of interest and should be made up of standard sources traceable to a nationally certified laboratory. In all radionuclide measurements, the volumes, shape, physical and chemical characteristics of the samples, standards and their containers must be as identical as practicable for the most accurate results.

B. Energy calibration.

The energy calibration (channel number of the MCA versus the γ -ray energy) of the detector system is accomplished at a fixed gain using standards containing known radionuclides. The standards should be in sealed containers and should emit at least four different γ -ray energies covering the range of interest, usually 50 keV to 2000 keV in order to test for system linearity. Some commercially available nuclides suitable for energy calibration are: ^{210}Pb , 46.5 keV; ^{241}Am , 59.5 keV; ^{109}Cd , 88 keV; ^{141}Ce , 145 keV; ^{51}Cr , 320 keV; ^{137}Cs , 662 keV; ^{54}Mg , 835 keV; ^{22}Na , 511 and 1275 keV; ^{88}Y , 898 and 1836 keV; ^{60}Co , 1173 and 1332 keV; equilibrated ^{226}Ra , 186, 352, 609, 1120, and 1765 keV. A mixed γ -ray standard for energy and efficiency calibration is also commercially available. This standard can be obtained in solid form in a user supplied container. The radionuclide purity of the standards should be verified periodically to ensure against

accidental contamination or the presence of long-lived impurities by comparing the observed spectra with the spectra published in the literature.

A MCA should be calibrated to cover the range of interest. If the range is 50 to 2000 keV, the gain of the system should be adjusted until the ^{137}Cs photopeak, 662 keV, is about one-third full scale. Leaving the gain constant, locate at least three other photopeaks of different energies, covering the same range. Determine and record the MCA channel number corresponding to the maximum count rate for each of the four energies. Germanium detectors will have a linear relationship if the equipment is operating properly. Similarly, MCAs and NaI(Tl) detectors being produced today are capable of producing an almost linear energy response. Samples should not be analyzed if this relationship is not obtained. Follow the appropriate manufacturer input instructions for the determination of the slope and intercept. During each day in which the spectrometry system is being used to analyze samples, the above sequence of operation shall be repeated using at least two different energies. If the slope and intercept are essentially unchanged, the energy calibration data remain valid. If an appreciable change in the slope or intercept is evident, the entire calibration procedure must be rerun.

C. Photon detection efficiency calibration.

Accumulate an energy spectrum using sealed, calibrated radioactivity standards in a desired and reproducible counting geometry. At least 10,000 net counts (total counts minus the Compton continuum and ambient background) should be accumulated in each full-energy γ -ray peak of interest.

Correct the radioactivity standard source γ -ray emission rate for the decay from the time of standardization to the time at which the count rate is measured.

Calculate the full-energy peak efficiency E_f as follows:

$$E_f = N_p/N_g$$

where

E_f = full-energy peak efficiency (counts per γ -ray emitted),
 N_p = net γ -ray count in the full-energy peak of interest (cps), and
 N_g = γ -ray emission rate (rays sec^{-1}).

If the standard source is calibrated as to activity, the γ -ray emission rate is given by:

$$N_g = A \cdot P_g$$

where

A = number of nuclear decays per second, and

P_g = probability per nuclear decay for the γ -ray.

For Ge detectors, plot the values for the full-energy peak efficiency versus γ -ray energy. The plot will allow the determination of efficiencies at energies for which standards are not available, and will show that the algorithms used in computerized systems are providing valid efficiency calibrations.

Once the efficiencies have been determined, it is unnecessary to recalculate them unless there is a change in resolution, geometry, or system configuration.

SAMPLE MEASUREMENTS

After the spectrometer system has been set up, the energy and efficiency calibrations are performed, then the unknown sample can be measured.

Following the general concepts of quantitative analytical chemistry, transfer the sample to the specimen container and position it in the same manner as was done during system calibration.

Measure the sample for a period of time long enough to acquire a γ -ray spectrum which will meet the minimum acceptable counting uncertainty.

PEAK AREA CALCULATIONS

Spectral data obtained with a Ge detector are only corrected for background when these peaks may alter the final results. In many experiments, the background may not affect the results but is still monitored to ensure the integrity of the system.

The underlying aim of this procedure is to subtract the continuum or baseline from the spectral data where it underlies a photopeak of interest. For operator-directed calculations, the choice of the baseline level may be straightforward. The simplest way, using a plot of the spectral data, is to draw a straight line, using judgement and experience, that best describes the baseline. Then the baseline data can be read directly from the plot and subtracted.

Photopeaks lying on a sloping baseline or one with curvature will be analyzed, independent of the method, with increased uncertainty. Use of data from these peaks should be limited to those cases where there is no other alternative. Photopeaks that overlap with each other will also increase the uncertainty of the final result.

In order to determine nuclide concentrations, the photopeak areas corrected for background and interferences are divided by the count time and efficiency for the energy of the γ -ray being calculated to give photons sec^{-1} for the peak of interest. If, as is the case for some nuclides, the branching ratio is not accurately known and a direct calibration was made with the same nuclide, the branching ratio and efficiency will be one number that converts cps to Bq sec^{-1} for the nuclide and photopeak of interest. If not, the photons sec^{-1} are converted to disintegrations sec^{-1} by dividing the photons sec^{-1} by the photons per disintegration, for the nuclide and photopeak of interest. The results are then corrected for attenuation or decay, or both.

Canberra Industries MicroSampo Version 2.0 (a commercial software package) is used at EML to perform these calculations.

While the uncertainty due to counting and calibration may represent a significant proportion of the total uncertainty in the measurement, systematic uncertainties should be determined and included in the above calculation. Systematic uncertainties include, but are not limited to, reproducibility of sample position, peak analyses, decay calculations,

background subtraction, pulse pile-up, cascade summing corrections, and self-absorption corrections.

ANALYSIS OF COMPLEX MIXTURES OF NUCLIDES WITH NAI(Tl) DETECTORS

Because of the inherent energy resolution of NaI(Tl) detectors, γ -ray peaks in complex mixtures of nuclides may not be separated sufficiently for quantification as outlined above. It may not even be possible to visually locate individual peaks if their energies are similar or their intensity is too low in relation to other γ -rays present in the spectrum. Complex mixtures of as many as 10 to 20 radionuclides can be quantified mathematically with computer programs using linear least squares techniques.

When using these techniques, care should be given to the following parameters.

A. System gain and zero energy channel.

The exact gain and zero energy channel of the spectrometer must be monitored and recorded. If the computer analysis program performs gain and/or baseline (zero energy channel) corrections on sample data, then the library of standards data must be obtained under uniform and precise calibration conditions.

B. Library standards.

The least squares analysis technique is a linear combination of all of the data contained in the standards library. Therefore, the standards library must contain a spectra of every component in the sample; in addition, these spectra must be obtained from the purest radionuclides available.

C. Counting of library standards.

All γ -ray spectra will contain a background component. The activity of the library standards must be high enough so that this background component will be insignificant, even though all computer programs make some kind of a background correction.

The duration of the counting period for the standard library spectra should be long enough to obtain statistically valid data, but it should be short enough so that analyzer gain and baseline drifts are insignificant.

The activity of the library standards should be chosen so that the counting rates of the predominant photopeaks are all about the same.

A very important data evaluation technique to be used with a least squares program is a superimposed plot of the original sample data and the computed spectral data. A plot of residuals (the difference between the original and computed spectra) is also very important. The residuals plot is very sensitive to errors that are caused by omitting radionuclides present in the sample from the library standards.

SAMPLE MEASUREMENTS

After the spectrometer system has been set up, the energy calibrations performed, and individual pulse-height spectra for nuclides expected to be present in samples are obtained, then the unknown specimens can be measured and quantified.

Following the general concepts of quantitative analytical chemistry, transfer the sample to the specimen container and position it in the same manner as was done during system calibration. Measure the sample for a period of time long enough to acquire a γ -ray spectrum which will meet the minimum acceptable counting uncertainty.

COMPUTER CALCULATIONS

WLSQ is an EML least squares Fortran computer program that can be run on a VAX or IBM-compatible PC to resolve complex spectra.

Systematic uncertainties include, but are not limited to: reproducibility of sample position, peak analyses, decay calculations, background subtraction, pulse pile up, cascade summing operations, and self-absorption corrections.

The uncertainty obtained from the least squares analysis can be substituted for the uncertainty in counting and should be included to obtain an overall uncertainty of the analysis. The uncertainties obtained from the least squares analysis are the square roots of the diagonal elements of the inverse matrix used to solve the linear set of simultaneous equations representing the sample spectra.

QUALITY CONTROL

The following quality control procedures are required so that the γ -ray spectrometers maintain their energy calibrations. In addition, the systems are to be monitored so that degradation in performance will be noticed as soon as possible.

A. Daily calibration checks.

The energy calibration of each Ge γ -ray detector is determined daily with a mixed nuclide source consisting of ^{241}Am and ^{60}Co .

In order to maintain an energy calibration of 0.5 keV/channel, count the Am-Co source to obtain well-defined peaks. The 59.5 keV γ -ray line from ^{241}Am should fall in channel 119. The 1332.5 keV γ -ray line from ^{60}Co should fall in channel 2665.

If the ^{241}Am and ^{60}Co peaks do not fall in the correct channels, first adjust the DC offset of the amplifier so that the 59.5 keV γ -ray line falls in channel 119. Then adjust the fine gain of the amplifier so that the 1332.5 keV γ -ray line falls in channel 2665.

Recount the Co-Am calibration standard to verify the peak positions and readjust the amplifier if necessary.

The energy calibration of each NaI(Tl) γ -ray detector is determined daily with a nuclide source consisting of ^{207}Bi .

In order to maintain an energy calibration of 10 keV/channel, count the ^{207}Bi source to obtain well-defined peaks. The 570 keV γ -ray line should fall in channel 57. The 1064 keV γ -ray line should fall in channel 106.

If the ^{207}Bi peaks do not fall in the correct channels, first adjust the DC offset of the amplifier so that the 570 keV γ -ray line falls in channel 57. Then adjust the fine gain of the amplifier so that the 1064 keV γ -ray line falls in channel 106.

Recount the ^{207}Bi calibration standard to verify the peak positions and readjust the amplifier if necessary.

B. Weekly efficiency calibration and resolution checks.

Each week the same ^{137}Cs calibration standard is counted, recorded, analyzed, and the date is entered into a permanent data base for each γ -ray spectrometry system.

Count the ^{137}Cs calibration standard in the same manner as unknown samples. Record the data for permanent storage and perform the usual data reduction analysis.

Enter the results of the analysis (Bq) and the resolution of the ^{137}Cs peak (full width at half maximum in keV) in the γ -quality control data base.

Report any deviation from the expected values before samples are analyzed. If remedial action is necessary, the cause and solution of the problem must be recorded in the laboratory logbook. A complete recalibration must be performed if any remedial actions have been taken.

4.5.3 Quality Control and Detection Limits

4.5.3 QUALITY CONTROL AND DETECTION LIMITS

QUALITY CONTROL

Quality control (QC) must be included in all aspects of a radiochemical measurement, from the collection of samples to the reporting of data. The exact QC practices that are to be used as part of the radiochemical procedures will vary somewhat, depending upon the chemical and radiological characteristics of the analyte. Some of the general requirements of a QC system for procedures are described here. Where the peculiarities of an analyte necessitate that modifications be made in these requirements, these modifications are discussed in the subsection after the analytical procedure for that analyte. The QC procedures described here are termed "internal" in that they are initiated by the analyst. Similarly, "external" QC procedures should be initiated by project leaders introducing QC samples "blind" into the sample stream. Data from both the internal and external QC procedures must be maintained and tabulated by the party initiating the procedures to document the continuing adequacy of the analytical work.

The QC practices used during radiochemical analyses are intended to assure the analyst that the determinations are under control. They involve continuous testing of those processes that influence the extent to which the results of the analyses remain within the required limits of precision and accuracy. The QC samples that are analyzed consist of five types: instrument calibration standards, blank samples, control samples, "spiked" samples, and replicate samples.

Instrument calibration standards are certified reference materials used primarily to calibrate the measurement apparatus. Standards for radioactivity measurements are discussed in Section 4.5.2. A key requirement of such materials is that they be traceable to the National Institute of Standards and Technology or to other recognized organizations.

Blank samples are commonly "reagent blanks" that are prepared by beginning with deionized water or an empty sample container. All appropriate reagents are added to the sample in the proper sequence and the normal steps involved in the analysis are followed. Ideally, the blank samples would be the same matrix as the routine sample but without the

analyte of interest. Normally, the activity of each routine sample is corrected by subtracting the reagent blank activity from it to obtain net activity. All the uncertainties of the measurements obtained throughout the analytical procedure should be propagated when calculating the uncertainty of the final result. However, very often only the Poisson errors of the counts of the reagent blank and of the sample are propagated when they are the most significant contributors to the total uncertainty.

Control samples contain known concentrations of the analyte. If possible, they should be the same matrix as the routine samples, and they should have concentrations in the same range as the routine samples. They usually are samples that are included by the analyst in the sample batches to be analyzed, and their values should be known with an uncertainty better than that which will be required of measurements of the routine samples.

"Spiked" samples are prepared by adding a known amount of the radionuclide of interest to blank samples or to samples that have already been analyzed in order to provide a matrix with a known activity.

Replicate samples usually consist of two or more aliquots of homogeneous solid, liquid or gas samples. Individual samples that are measured by nondestructive techniques, such as γ -ray spectrometry, may be measured more than once to obtain replication of the data.

Analytical instruments, such as analytical balances, must be calibrated regularly. The standards that are used to calibrate any instrument should be traceable to the National Institute of Standards and Technology (NIST), when possible. A record of instrument performance must be maintained by the instrument operator. A record must be kept of any modifications that are made in an instrument, and such modifications must be approved by the analyst's supervisor beforehand and must conform to the safety standards and practices that are specified in the EML Safety Manual.

For most radiochemical procedures, QC samples are added to make up between 10-20% of the sample stream. It is good analytical practice to process high-level and low-level samples in independent batches whenever possible to minimize the possibility of cross contamination. When samples of very low activity are to be analyzed, blank sample analyses and instrument background measurements should be increased.

The best estimates of a reagent blank or blank sample activity, instrument background count rate and detection efficiency are obtained from the mean value of replicate determinations. Whenever possible, the mean and standard error of the replicate determinations should be used in calculating a final value.

ESTIMATING THE LOWER LIMIT OF DETECTION

Counting data are like other analytical data in that a series of measurements of background, for example, should show a Gaussian distribution like that in Figure 1. The standard deviation (SD) for the distribution will give an estimate of how well additional background measurements will approach the original mean. In most environmental analyses, however, we cannot afford the luxury of multiple analyses or even duplicates. Fortunately, counting data follow the Poisson distribution and it is possible to estimate the SD from a single measurement. This SD of counting can be used in the same way as the Gaussian SD to establish a confidence interval about the mean value. For example, if the confidence interval chosen is ± 1 SD, additional measurements should fall into this interval 68% of the time. An interval of ± 2 SD would contain the new value 95% of the time.

Thus, if we establish a background with its associated SD for a counting system, this should give us a way of estimating our lower limit of detection (LLD). For example, a sample count > 1 SD above background should indicate the presence of activity 84% of the time. In the other 16%, there would be a false positive. If the limit of 2 SD is used, the values would be 97.5% real and 2.5%, false with 3 SD, 99.85% and 0.15%. This seems to be very simple, but it does not consider the fact that the sample counts also would have a distribution.

The interaction of the two distributions becomes more important as environmental analyses tend toward lower levels of radioactivity. As the activity decreases, the counter background or method blank has to be subtracted from the gross count, and estimating the precision of these measurements and also the limit of detection for a procedure becomes slightly more difficult. Where the total count on a sample approaches the background count, you have a situation as in Figure 2 where the two distributions overlap. [This form of showing the detection limit for counting was given by Healy (1956).]

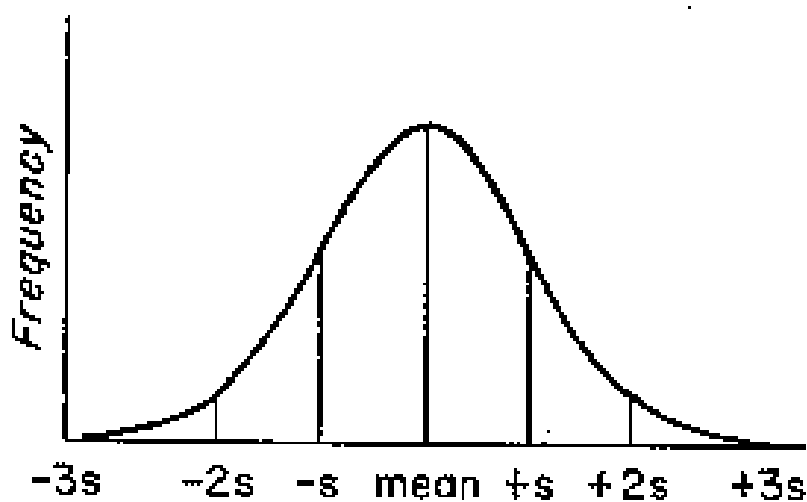


Figure 1. Distribution curve where the relative areas show the fraction of results that should be included within $\pm s$ (0.68), $\pm 2 s$ (0.95) and $\pm 3 s$ (0.997).
Intersecting distributions for background and sample count rates.

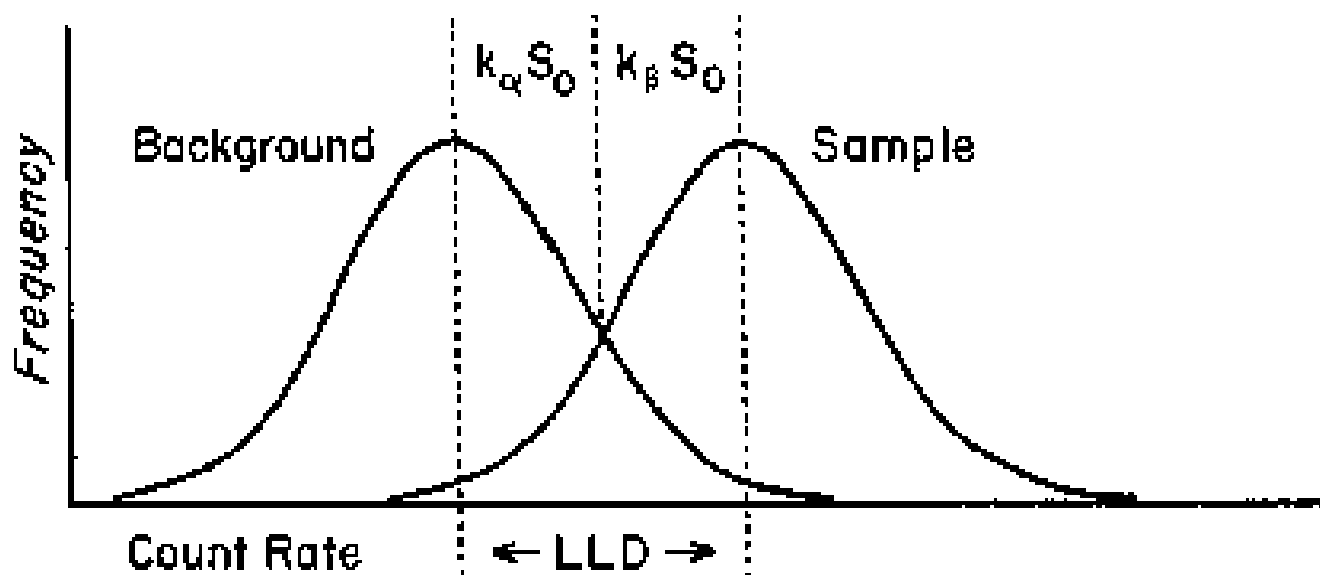


Figure 2.

Pasternack and Harley (1971) developed a procedure for calculating what they defined as the LLD, the smallest amount of sample activity that will yield a net count for which there is a confidence at a predetermined level that activity is present. This concept was only practical for γ counting in the original form since they required that the number of counts be sufficient for the Poisson distribution to approach the Gaussian distribution so that Gaussian statistics could be used.

However, the approximation is valid down to a few total counts. Thus, the calculations can be applied to any detection system.

The LLD can be approximated as

$$LLD \cong (k_{\alpha} + k_{\beta})s_0$$

where

k_{α} is the value for the upper percentile of the standardized normal variate corresponding to the preselected risk for concluding falsely that activity is present (α),

k_{β} is the corresponding value for the predetermined degree of confidence for detecting the presence of activity ($1 - \beta$), and

s_0 is the estimated standard deviation for the net sample activity.

A still shorter approximation may be made if the values of α and β are set at the same level and if the gross activity and background are very close. In this case:

$$s_0 = \sqrt{s_{\text{gross}}^2 + s_{\text{bkg}}^2} = s_b \sqrt{2}$$

The equation then becomes,

$$LLD \cong 2k s_{\text{bkg}} \sqrt{2}$$

The values of k for common α 's are:

α	$1-\beta$	k	$2k\sqrt{2}$
0.01	0.99	2.327	6.59
0.02	0.98	2.054	5.81
0.05	0.95	1.645	4.66
0.10	0.90	1.282	3.63
0.20	0.80	0.842	2.38
0.50	0.50	0.000	0.00

Routinely, an α value of 0.05 is used at EML for calculating the LLD. The LLD will be provided at the end of each procedure, if appropriate.

The simplest possible case is one where the sample activity is zero. It is sometimes not realized that if a series of counts is taken on such a system, that half of the net values should be less than zero. Negative counts are not possible, of course, but when there is a blank or a background, the entire scale is shifted up and the situation becomes one where half of the sample counts on a zero activity sample would be less than background. This negative net count occurs frequently in low-level measurements, causing considerable concern, but such results are to be expected.

Thus, if we have a counter with a background of 0.003 counts sec^{-1} (cps) and we count the sample and background for 24000 sec, then

$$s_b = \sqrt{72} = 8.5$$

If we set α at 0.05, accepting a 5% chance of a false positive result for a sample having no activity,

$$\text{LLD} = (4.66)(8.5) = 40 \text{ counts}$$

or ~ 0.002 cps.

Since the simplified formula used sets $k_{\alpha} = k_{\beta}$, we are also accepting the chance that we will detect activity when it is present, 95% of the time, but will miss it 5% of the time.

If a 50% chance of finding activity is accepted, the LLD is zero. This is to be expected from the previous qualitative description.

The original paper of Pasternack and Harley (1971) applied the LLD concept to multicomponent γ spectrometry with NaI detectors. They noted particularly the decrease in sensitivity as the number of components in the mixture increased, and observed a decrease when the number of radionuclides in the library was increased, even when the actual sample contained only a single component.

Multicomponent α spectrometry can be performed in accordance with the procedures of Fisenne et al. (1973). Solid state α -spectrometry calculations are simpler, since overlapping spectra are less common. The basic principle is that an interfering radionuclide effectively increases the background for the nuclide sought.

Examples of LLD calculations for three typical measurement situations are given for illustrative purposes in the appendix.

ZERO LEVELS

A. Introduction.

When the measurement of background yields a positive value, its variance and SD may be calculated based on Poisson counting statistics. In any subsequent measurement of a sample, the net activity and its SD may be evaluated to determine whether significant radioactivity is present.

A special case arises when neither counter background nor sample activity is detectable over a reasonably long counter interval. It is of practical interest to be able to quantitate the upper limit of radioactivity that could be present in this sample and yet yield this result, since increasingly more environmental nuclide measurements may fall into this category.

The measurement and identification of low levels (< 0.0001 Bq)/sample) of α -emitting nuclides by spectrometry represents a specific example. This measurement is performed with a silicon surface barrier or ion implant detector. Any background counts measured in these detectors usually fall within the energy intervals corresponding to naturally occurring nuclides, primarily radium and its progeny. The background count rate for these detectors usually ranges from 0-5 counts per 6×10^4 sec in any of the energy intervals containing peaks of the U series, Pu isotopes and most other α emitters of interest.

Thorium-232 is a special case, since the energy interval at which it appears (3.9 MeV) normally exhibits very low background. For example, a measurement for ^{232}Th yielded zero counts in 3×10^5 sec and zero background counts over a similar count interval. It is of value to calculate rigorously an upper limit of ^{232}Th activity which could be present in such a sample. Two examples are given here. One, where the counting interval is fixed and the other where the count time can be calculated based upon a desired fixed value for the upper limit of activity in the sample (Harley and Fisenne, 1976).

B. Predetermined count interval.

We may apply the binomial distribution to a group of N_0 atoms to calculate the probability that there will be no α decays in counting interval, t .

The binomial distribution for the probability of x number of disintegrations out of a total of N_0 atoms is:

$$\text{Pr}(x) = \frac{N_0!}{(N_0 - x)! x!} p^x q^{(N_0 - x)} \quad (1)$$

where

- $\text{Pr}(x)$ = probability of x disintegrations during time, t ,
- N_0 = initial number of radioactive atoms,
- p = probability that an atom will decay in time, t , and
- q = probability that an atom will not decay in time, t .

Since the probability, q , that an atom will not decay is:

$$q = e^{-\lambda t}$$

then,

$$p = (1 - e^{-\lambda t})$$

and

$$\text{Pr}(x) = \frac{N_0!}{(N_0 - x)! x!} (1 - e^{-\lambda t})^x (e^{-\lambda t})^{N_0 - x}$$

The probability of no disintegrations in time t is then:

$$\text{Pr}(0) = \frac{N_0!}{N_0 0!} (1 - e^{-\lambda t})^0 (e^{-\lambda t})^{N_0} = e^{-\lambda N_0 t} \quad (2)$$

Because the detector efficiency is $<100\%$, there is also the possibility that one or more disintegrations occur but that they are not detected. If the detector efficiency is G and one disintegration occurs, the probability of no count being detected is $(1-G)$. If two disintegrations occur, the probability of zero counts is $(1-G)^2$. In general, whenever x disintegrations occur, the probability that zero counts will be seen is $(1-G)^x$. Then the probability that one or more of N_0 atoms present disintegrates during time, t , but that none is detected is:

$$\text{Pr}(1) \cdot (1 - G) + \text{Pr}(2) \cdot (1 - G)^2 + \text{Pr}(3) \cdot (1 - G)^3 + \dots \quad (3)$$

From (1), the probability of one disintegration occurring is:

$$\text{Pr}(1) = \frac{N_0!}{(N_0 - 1)! 1!} (1 - e^{-\lambda t})^1 (e^{-\lambda t})^{N_0 - 1} \quad (4a)$$

The probability of two disintegrations occurring is:

$$\text{Pr}(2) = \frac{N_0!}{(N_0 - 2)! 2!} (1 - e^{-\lambda t})^2 (e^{-\lambda t})^{N_0 - 2} \quad (4b)$$

and so on.

If the assumption can be made that t is small and that N_0 is much greater than one, then $\text{Pr}(1)$, $\text{Pr}(2)$, etc., simplify to:

$$\text{Pr}(1) \cong N_0 (\lambda t)^{-1} (e^{-\lambda N_0 t}) \quad (5a)$$

$$\text{Pr}(2) = \frac{N_0 N_0}{2!} (\lambda t)^2 (e^{-\lambda N_0 t}) \quad (5b)$$

$$\text{Pr}(3) = \frac{N_0 N_0 N_0}{3!} (\lambda t)^3 (e^{-\lambda N_0 t}) \quad (5c)$$

The probability for observing zero counts is the sum of the probabilities for no disintegration to occur plus those for the occurrence of one or more disintegrations which are not detected.

$$P = \text{Pr}(0) + \text{Pr}(1) \cdot (1 - G) + \text{Pr}(2) \cdot (1 - G)^2 + \text{Pr}(3) \cdot (1 - G)^3 + \dots$$

$$\begin{aligned} &\cong e^{-\lambda N_0 t} + \lambda N_0 t e^{-\lambda N_0 t} (1 - G) + \frac{[\lambda N_0 t (1 - G)]^2}{2!} e^{-\lambda N_0 t} + \dots \\ &\cong e^{-\lambda N_0 t} \left[1 + \frac{\lambda N_0 t (1 - G)}{1!} + \frac{[\lambda N_0 t (1 - G)]^2}{2!} + \frac{[\lambda N_0 t (1 - G)]^3}{3!} + \dots \right] \\ &\cong e^{-\lambda N_0 t} \cdot e^{+\lambda N_0 t (1 - G)} \end{aligned} \quad (6a)$$

$$\cong e^{-\lambda N_0 t G} \quad (6b)$$

$\lambda N_0 t G$ is the number of counts to be expected during the interval t .

We would like the occurrence of zero counts, when activity is actually present, to have a small probability. If this probability is arbitrarily set to 0.05 so that zero counts will be detected only 5% of the time, when N_0 atoms are actually present and the counting interval is t minutes, then (6b) becomes:

$$e^{-\lambda N_0 t G} = 0.05$$

$$\lambda N_0 t G = -\ln(0.05)$$

$$(\lambda N_0) = A_0 = -\frac{1}{t G} \ln(0.05) \quad (7)$$

$$A_0 = \frac{3}{t G}$$

where $\lambda N_0 = A_0$ is the upper limit of sample activity in Bq at the 95% confidence level, when t is in seconds and G is expressed as fractional efficiency.

C. Predetermined upper limit of activity.

It may be of interest to establish the counting time required to determine that a chosen upper limit of activity is present. Solving (7) for the counting time yields:

$$t = \frac{3}{A_0 G} \quad (8)$$

As an example, the measured data for the ^{232}Th sample will be used. The efficiency of the surface barrier detector is 0.30 and zero counts were recorded in 3×10^5 sec. From (7):

$$A_0 = \frac{3}{(3 \times 10^5) (0.3)} = 3 \times 10^{-5} \text{ Bq} \quad (9)$$

The upper limit of activity in this sample is thus 3×10^{-5} Bq at the 95% confidence level.

BACKGROUND NOT ZERO

All of the above expressions apply equally well to background activity. It is possible that either a background count did not occur during the count interval or that one or more occurred but were not detected. In this case, the upper limit to background activity is the same as that calculated in (9), except that there is no efficiency for background and the background activity is expressed as counts sec^{-1} . Expression (9) would then become:

$$A_0 G = \frac{3}{(3 \times 10^5)} = 1 \times 10^{-5} \text{ counts sec.}^{-1}$$

Then according to the convention at EML, any value of net activity equal to zero would be evaluated in comparison with:

$$S_{\text{net}} = \sqrt{\frac{1 \times 10^{-5}}{3 \times 10^{-5}} + \frac{1 \times 10^{-5}}{3 \times 10^{-5}}} = 8 \times 10^{-6} \text{ counts sec}^{-1}$$

and the activity would be reported as:

$$\frac{\leq 8 \times 10^{-6}}{0.3},$$

or $\leq 2 \times 10^{-5}$ Bq at the 95% confidence interval.*

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"Reporting Results of Radioactivity Measurements at Near Zero Levels of Sample Activity and Background"

USERDA Report HASL-306, pp. 43-50 (1976)

Healy, J. W.

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USAEC Report WASH-736, September (1957)

*This convention would be used for reporting single values. For averaging purposes, the actual value of the net activity, positive or negative, would be used.

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"Detection Limits for Radionuclides in the Analysis of Multi-Component Gamma Ray
Spectrometer Data"

Nuclear Inst. and Methods, 91, 533-540 (1971)

APPENDIX

LOWER LIMIT OF DETECTION*

In the analyses of samples for naturally occurring radionuclides, it is rare that the sample activity and background are the same. Reagent blanks processed through the chemical procedure will show activity in excess of the background of the detection system. Multiple measurements of the background and multiple reagent blank analyses are used to obtain the respective standard errors of these variables. In this case, the equation is

$$S_s = [s_{\text{gross}}^2 + s_{\text{BK}}^2 + s_{\text{BI}}^2]^{1/2} \quad (1)$$

where

s_{gross} = the mean background plus mean reagent blank counts for a specified counting time,

s_{BK} = the standard error of the background from multiple measurements (n), corresponding to the same counting time as above, $([s_{\text{BK}}^2]/[n])^{1/2}$, and

s_{BI} = the standard error of the blank from multiple analyses (n), also with the same counting time, $([s_{\text{BI}}^2]/[n])^{1/2}$.

Then, the LLD at the 95% confidence level is

$$\text{LLD}_{95\%} = (k_\alpha + k_\beta) S_s = 3.29 S_s \quad (2)$$

where

k_α = the preselected risk for concluding falsely that activity present. At the 95% confidence level (α) = 1.645, and

k_β = the predetermined degree of confidence for detecting the presence of activity. At the 95% confidence level $(1-\beta) = 1.645$.

* Taken from Pasternack and Harley (1971).

Thus, at $LLD_{95\%}$

$$k_{\alpha} = k_{\beta} = 1.645$$

and

$$(k_{\alpha} + k_{\beta}) = 3.29$$

The $LLD_{95\%}$ must be converted to activity (Bq) using the appropriate conversion factors.

$$LLD_{95\%} \text{ (Bq)} = \frac{3.29 s_s}{(CT)(\epsilon)(Y)} \quad (3)$$

where

CT = the counting time or counting interval in seconds,

ϵ = the detection efficiency of the measurement system (counts sec^{-1} Bq $^{-1}$), and

Y = the average radiometric or chemical yield obtained for the separation method.

The applications of Equations 1 and 3 to solid state α -spectrometry measurements are illustrated below.

In ^{239}Pu measurements, a manmade radionuclide, there is no measurable blank and the mean background count from multiple measurements is used. Then, the term s_{Bl} does not appear and Equation 1 reduces to

$$s_s = [s_{\text{gross}} + s_{\text{Bk}}^2]^{1/2} \quad (4)$$

For this situation s_{gross} is the mean background counts and s_{Bk} is the standard error of multiple measurements.

Given the following variables:

counter efficiency:	40%
counter background	
(in the ^{239}Pu energy region):	$3.3 \times 10^{-5} \pm 1.7 \times 10^{-5} \text{ counts sec}^{-1}$ $(0.002 \pm 0.001 \text{ counts min}^{-1})$
tracer yield:	75%
counting time:	60,000 s (1,000 min)

$$s_s = (2 + 1 \text{ counts})^{1/2} = (3 \text{ counts})^{1/2} \quad (5)$$

and

$$\text{LLD}_{95\%} = \frac{3.29(3 \text{ counts})^{1/2}}{(60000 \text{ sec})(0.40 \text{ counts sec}^{-1} \text{ Bq}^{-1})(0.75 \text{ yield})} = 0.0003 \text{ Bq}$$

In ^{210}Po measurements there usually is a measurable blank and all variables in Equation 1 must be taken into account.

Given the following variables:

counter efficiency:	40%
counter background	
(in the ^{210}Po energy region):	$8.3 \times 10^{-5} \pm 5.0 \times 10^{-5} \text{ counts sec}^{-1}$ $(0.005 \pm 0.003 \text{ counts min}^{-1})$
blank:	$1.6 \times 10^{-4} \pm 1.0 \times 10^{-4} \text{ Bq}$ $(5.0 \times 10^{-5} \pm 3.3 \times 10^{-5} \text{ counts sec}^{-1})$ $(0.003 \pm 0.002 \text{ counts min}^{-1})$
tracer yield:	80%
counting time:	60,000 s (1,000 min)

Again, mean background from multiple measurements and the mean reagent blank from multiple analyses are to be used.

$$s_s = [(5+3 \text{ counts}) + (2 \text{ counts})^2 + (3 \text{ counts})^2]^{1/2} = 4.6 \text{ counts}$$

$$\text{LLD}_{95\%} = \frac{3.29(4.6 \text{ counts})}{(60000 \text{ sec})(0.40 \text{ cps Bq}^{-1})(0.80 \text{ yield})} = 0.0008 \text{ Bq}$$

The LLD can be reduced by: (1) increasing the number of background and reagent blank measurements, assuming these do not increase over time; (2) increasing the counting time; (3) increasing the counting efficiency; and (4) increasing the sample yield.

4.5.4 Radiochemical

Americium

Am-01-RC

AMERICIUM IN SOIL

Contact Person(s) : Anne Berne

APPLICATION

This procedure is applicable to soils which contain americium deposited from worldwide fallout and some nuclear activities.

Americium is leached from the soil with HNO_3 and HCl and simultaneously equilibrated with ^{243}Am tracer. The soil is processed through the plutonium separation steps using ion exchange resin according to Procedure Pu-11-RC. If determination of plutonium is desired, an appropriate plutonium tracer should be added along with the ^{243}Am tracer. Americium is collected with a calcium oxalate precipitation and finally isolated and purified by ion exchange. After source preparation by microprecipitation, the ^{241}Am is determined by alpha spectrometry using ^{243}Am tracer to provide recovery data.

SPECIAL APPARATUS

1. For microprecipitation, see Procedure G-03.
2. Ion-exchange columns - see Specification 7.5.

SPECIAL REAGENTS

1. Americium-243 tracer solution, about 0.15 Bq g^{-1} in dispensing bottle - standardize for total disintegration rate. Measure purity on an α spectrometer.

2. Bio-Rad AG 1-X8 resin (100-200 mesh) - see Specification 7.4.
3. Bio-Rad AG 1-X4 resin (100-200 mesh) - see Specification 7.4.
4. 4M ammonium thiocyanate solution - dissolve 304 g of NH_4SCN in deionized distilled water and dilute to 1 L. To purify the 4M NH_4SCN , place 4 L of solution in a 5 L polyethylene beaker. Add 25 mL of Bio-Rad AG 1-X4 resin (100-200 mesh) ion exchange resin, and mix for 1 h with a magnetic stirrer. Allow the resin to settle and filter by gravity through Whatman No. 40 filter paper. Repeat the addition of the resin and filtration steps twice more to remove all Fe^{+3} from the 4M NH_4SCN . Store the purified 4M NH_4SCN in a polyethylene bottle.
5. 0.4M NH_4SCN - 0.3M HCl - dilute 100 mL of purified 4M NH_4SCN to 500 mL with water, then add 25 mL HCl and dilute to 1 L. Make 2 L of solution for 10 samples.
6. Calcium carrier solution, 100 mg mL^{-1} - dissolve 25 g CaCO_3 in a minimum of HNO_3 and dilute to 100 mL.
7. Iron carrier, 100 mg mL^{-1} - slowly heat 100 g of iron powder in 500 mL of HCl until reaction ceases. Carefully and slowly add 100 mL of HNO_3 while stirring. Cool and dilute to 1 L.
8. Oxalate wash solution - dissolve 10 g of oxalic acid to make 1 L of solution (~ 1% solution).

SAMPLE PREPARATION

1. Weigh 1000 g of soil into a 4-L beaker. Add a weighed amount (about 0.03 Bq) of ^{243}Am tracer.
2. Slowly add 900 mL of HNO_3 . Control the foam with the addition of a few drops of n-octyl alcohol. When the reaction subsides, add 300 mL of HCl . Allow the mixture to react at room temperature, then heat on a low temperature hot plate overnight with occasional stirring.

3. Dilute to 1:1 HNO_3 and filter through Whatman No. 42 filter paper into a 3-L flask. Wash with 1:1 HNO_3 . Retain the filtrate. Return the residue and filter to the original beaker.
4. Add 900 mL of HNO_3 and wet ash the filter paper. Maintain the HNO_3 volume. Cool and add 300 mL of HCl to the residue and heat on a low temperature hot plate for about 3 h with occasional stirring. Cool and allow to settle overnight.
5. Filter and wash as in Step 3. Combine the filtrate with the filtrate from Step 3. Return the residue and filter to the original beaker.
6. Repeat Step 4.
7. Filter and wash as in Step 3. Combine the three filtrates and discard the residue.
8. Decompose any organic matter in the extract by heating with repeated additions of HNO_3 , covering the sample with a watch cover and letting the sample reflux. Concentrate until salting out begins to occur. Add an equal volume of water. If solution is not clear, proceed to Step 9, otherwise go to Step 14.
9. If any siliceous matter is present, filter by gravity over an 18.5 cm Whatman No. 42 filter paper. Wash the residue with 1:1 HNO_3 . Reserve the filtrate.
10. Transfer the filter paper with the residue to the original beaker and ash the paper with 100 mL of HNO_3 . Repeat two or three times, then transfer the residue into a 100-mL platinum dish using 1:1 HNO_3 .
11. Add 5-25 mL of HF and 5-25 mL of HNO_3 to the platinum dish and evaporate on a medium temperature hot plate. Repeat the addition of the HF/HNO_3 and the evaporation process two or three times. Rinse the walls of the platinum dish with 1:1 HNO_3 and evaporate. Repeat three times. Evaporate to dryness. Dissolve with 1:1 HNO_3 and evaporate to dryness.
12. Dissolve the residue in 1:1 HNO_3 and filter by gravity through a Whatman No. 42 filter paper. Add the filtrate to the solution from Step 9. Discard the filter and any residue.

13. Heat the combined solution (with the addition of HNO_3 if necessary) to complete the oxidation of any organic materials. Evaporate to near dryness. Redissolve in 1:1 HNO_3 and stir to get a clear solution, adding 1:1 HNO_3 as necessary.
14. Proceed to Procedure Pu-11-RC, ion-exchange purification saving the column effluents for **Americium Determination**.

AMERICIUM DETERMINATION

1. Evaporate the americium effluents to incipient dryness. Redissolve in a minimum amount of 1:1 HNO_3 , dilute with four volumes of water.
2. Add 5 mL of calcium carrier solution (500 mg of calcium) and 50 g L^{-1} of oxalic acid to the sample while stirring with a magnetic stirrer. (The total volume of the sample solution can be estimated using the markings on the beaker, and the amount of oxalic acid to be added is calculated using that volume.)
3. Adjust the pH of the solution to 2.0 - 2.5 with NH_4OH using pH paper as an indicator and continue to stir for 30 min. Remove the magnetic stir bar.
4. Cool and let stand until precipitate settles and solution clears (for more than 6 h or overnight). Check for completeness of precipitation using a drop of saturated $\text{H}_2\text{C}_2\text{O}_4$ solution. Aspirate (or decant), using a disposable transfer pipette and suction, as much liquid as possible without disturbing the precipitate. Transfer the precipitate to a 250-mL centrifuge bottle using oxalate wash solution (see **Note 1**). Balance the bottles on a double pan balance and centrifuge for 10 min at 2000 rpm. Decant and discard the supernate.
5. Break up the precipitate with a stirring rod and wash the precipitate with the oxalate wash solution. Centrifuge, decant and discard the wash. Repeat wash. Redissolve the precipitate in a minimal amount (50-70 mL) of concentrated HCl (redissolve the precipitate in ~200 mL of HNO_3 a final time and proceed to Step 8). (**Note:** Dissolution is easier if the centrifuge bottle is placed in a hot water bath and stirred with a glass rod).

6. Transfer the dissolved precipitate to the original 600-mL beaker. Add enough water to make ~ 1M solution. Add 50 g L⁻¹ of oxalic acid.
7. Repeat Steps 3 through 6 until supernate is colorless.
8. Transfer the dissolved precipitate to the original beaker and heat to destroy the oxalate ion. Evaporate to near dryness. Dissolve in minimum 1:1 HNO₃. Transfer to centrifuge bottle using water to complete the transfer.
9. Add enough water to make ~1M HNO₃. Warm the solution in a 90° hot water bath and add 0.2 mL iron carrier solution (20 mg iron).
10. With the centrifuge bottle in the hot water bath adjacent to a hood, adjust the pH of the solution to 8-9 with NH₄OH while stirring with a glass rod. Allow solution to digest in a hot water bath for 20 min.
11. Cool in a cold water bath, rinse, and remove the glass rod. Balance the bottles on a double pan balance and centrifuge for 40 min at 2000 rpm.
12. Decant (or aspirate) and discard the supernate. Add 10 mL concentrated HCl to dissolve the Fe(OH)₃ pellet. Add four drops 30% H₂O₂ to oxidize any Mn present, followed by 100 mL of water. Heat in the water bath for 30 min to get rid of the excess H₂O₂.
13. Repeat Steps 10 to 12 three times. Reprecipitate, centrifuge and redissolve. The final precipitate should be redissolved in HNO₃.
14. Transfer to a 250-mL beaker, evaporate to dryness, add 20 mL HNO₃, and evaporate to dryness again.
15. Dissolve the wet-ashed residue in 40 mL 1:1 HNO₃. Cool in an ice-water bath. Add 0.6-1.0 g NH₂OH · HCl, dissolve, and let the solution react for 15 min. Cover with a watch glass. Heat on a low temperature hot plate to decompose unreacted NH₂OH · HCl, then bring to a gentle boil for 1-2 min. Cool and pass the solution through a 1:1 HNO₃ ion-exchange column (see **Note 2**). Collect the effluent in a 400-mL beaker. Wash the column with 150 mL of 1:1 HNO₃, and collect in the beaker.

16. Evaporate the sample in the 400-mL beaker to dryness. Convert to HCl by adding 20-30 mL of HCl at a time, heat to almost dryness, and repeat the HCl addition and evaporation at least three times. Evaporate again and dissolve the final residue in 30 mL of HCl. Pass this solution through a 12N HCl ion exchange column (see **Note 3**). Collect the effluent in a 250-mL beaker. Wash with 100 mL of HCl, and collect in the 250-mL beaker.
17. Evaporate to dryness. Dissolve in 1-2 mL of HCl. Cool thoroughly. Add 40 mL of 4M NH₄SCN and stir immediately. Stir the sample and pass the solution through a 4M NH₄SCN column (see **Note 4**). Discard the effluent.
18. Wash the column with 200 mL of 4N NH₄SCN solution. Discard the wash solution.
19. Elute the americium into a 250-mL beaker with 180 mL of 0.4N NH₄SCN - 0.3N HCl. Evaporate to dryness on a low temperature hot plate overnight. Discard the resin.
19. To remove NH₄⁺ salts, place the beaker on an iron tripod and heat slowly with a cool Bunsen flame. After ~ 0.5 h, increase the flame temperature and continue heating to remove all NH₄⁺ salts and S, then heat briefly to dull red heat. This step requires ~ 1-1.5 h.
20. Cool to room temperature. Add 25 mL of HNO₃ and boil slowly for a few minutes. **Cautiously** add 1 mL of 30% H₂O₂ and evaporate the solution to dryness.
21. Convert the residue to Cl⁻ by adding 1 mL of HCl and evaporating to dryness twice and proceed to microprecipitation.

Notes:

1. If a centrifuge is not available, centrifugation can be replaced by filtering and wet ashing the filter paper and precipitate in HNO₃
2. Preparation of 1:1 HNO₃ Column. Position a plug of glass wool at the base of an 11-mm o.d. column. Transfer with deionized distilled water, 15 mL of wet settled Bio-

Rad AG 1-X8 resin (100-200 mesh) to the column and allow it to settle. Place a second plug of glass wool on top of the resin and with the stopcock open allow the H₂O level to reach the top of the upper plug. Pass 150 mL of 1:1 HNO₃ through the resin bed in three 50-mL portions or enough so that the effluent tests free of Cl⁻ ion using dilute silver nitrate solution, allowing the level of each portion to reach the top of the upper glass wool plug.

3. Preparation of HCl Column. Position a plug of glass wool at the base of an 11-mm o.d. column. Transfer 10 mL of wet settled Bio-Rad AG 1-X4 resin (100-200 mesh) with deionized water to the column and allow it to settle. Place a second plug of glass wool on top of the resin and with the stopcock open allow the H₂O level to reach the top of the upper plug. Pass two 50-mL volumes of HCl through the resin bed and allow each to reach the top of the upper glass wool plug.
4. Preparation of NH₄SCN Column. Position a plug of glass wool at the base of an 11-mm o.d. column. Transfer with deionized distilled water, 15 mL of wet settled Bio-Rad AG 1-X4 resin (100-200 mesh) to the column and allow it to settle. Place a second plug of glass wool on top of the resin and with the stopcock open allow the H₂O level to reach the top of the upper plug. Pass 100 mL of purified 4M NH₄SCN through the resin bed in two 50-mL portions, allowing the level of each portion to reach the top of the upper glass wool plug.

MICROPRECIPITATION

See Microprecipitation Source Preparation for Alpha Spectrometry, Procedure G-03.

DATA PROCESSING AND ANALYSES

For alpha spectrometry measurements, please see Procedure A-01-R.

LOWER LIMIT OF DETECTION (LLD)

Counter Efficiency	(%)	25
Counter Background	(cps)	15×10^{-6}
Yield	(%)	50
Blank	(cps)	-
LLD (400 min)	(mBq)	1
LLD (1000 min)	(mBq)	0.5
LLD (5000 min)	(mBq)	0.3

Am-02-RC

AMERICIUM-241 IN SOIL - GAMMA SPECTROMETRY

Contact Person(s) : Colin G. Sanderson

APPLICATION

This procedure is capable of determining small amounts of ^{241}Am in large volume soil samples. The lower limit of detection for 600-800 g of soil in a Marinelli beaker is 0.74 mBq for a 1000-min count.

Americium-241 decays with the emission of γ rays at 11.9, 13.9, 17.8, 20.8, 26.4, and 59.5 keV. The 59.5 keV γ ray, which has an abundance of 35.9%, can be measured in soil with commercially available germanium (Ge) semiconductor γ -ray detectors and 600 mL Marinelli beakers. Gamma-ray attenuation corrections are required if the calibration source and the sample are in a different matrix or are of different densities.

SPECIAL APPARATUS

1. Hyperpure Ge γ -ray detector, shield, and associated electronics.
2. Multichannel analyzer.
3. Marinelli beaker - see Specification 7.22.

SPECIAL REAGENT

Americium-241 calibration solution, about 2.50 Bq mL⁻¹.

SPECTROMETER CALIBRATION

1. Transfer 600 mL of standardized ^{241}Am solution to a Marinelli beaker.
2. Set the spectrometer energy calibrations at 0.5 keV/channel and count the standard until 10,000 or more counts are accumulated in the channels corresponding to 58.0 to 61.5 keV.
3. Record the count time and the channel-by-channel data corresponding to 56.0 to 63.5 keV.

SAMPLE PREPARATION

1. Transfer 600 mL of prepared soil to a Marinelli beaker.
2. Accumulate sufficient counts in the 59.5 keV ^{241}Am peak to achieve the desired counting statistics.
3. Record the count time and the channel-by-channel data corresponding to 56.0 to 63.5 keV.

DETERMINATION

If computer calculation techniques are used to determine peak areas from spectral data, the same techniques must be used for both calibration standards and samples. However, in most instances, simple peak integration by channel summing is sufficient.

The net count in the ^{241}Am peak = $A - B - C$.

where

A = sum of counts in the 8 channels from 58.0 to 61.5 keV

B = sum of counts in the 4 channels from 56.0 to 57.5 keV

C = sum of counts in the 4 channels from 62.0 to 63.5 keV

B and C are the leading and trailing edges of the photopeak and represent the background upon which the photopeak is superimposed.

The net ^{241}Am counts, AmC, corrected for attenuation equals

$$A/e^{-(\mu d \cdot w)}$$

where

A = observed net counts in the ^{241}Am peak,

μd = attenuation constant for Marinelli beaker (see Note below),
for H_2O , $\mu d = 0.000427 \text{ cm}^2 \text{ g}^{-1}$
for soil, $\mu d = 0.000533 \text{ cm}^2 \text{ g}^{-1}$

w = weight in g of the standard or sample.

The ^{241}Am detector efficiency at 59.5 keV,

$$\text{Efficiency} = (\text{AmC}/t)/(\text{Ac} \cdot 600)$$

where

AmC = net ^{241}Am counts of the standard, corrected for attenuation, and

t = standard count time (sec).

Ac = ^{241}Am activity of standard (Bq mL^{-1}).

The $\text{Bq } ^{241}\text{Am}$ in the sample = $(\text{AmC}/t)/\text{Efficiency}$

where

$AmC =$ net ^{241}Am counts of the sample, corrected for attenuation, and

$t =$ sample count time (sec).

Note:

The Marinelli beaker attenuation constant ($\mu_d = 0.000533 \text{ cm}^2 \text{ g}^{-1}$) is for soil of normal composition. Soils or ores composed of high atomic number elements will require a different constant. For example, a 1% U ore will attenuate the 59.5 keV γ ray to 7% more than normal soil and the correct μ_d would be $0.000677 \text{ cm}^2 \text{ g}^{-1}$.

Am-03-RC

AMERICIUM IN WATER, AIR FILTERS, AND TISSUE
(see Volume II)

Am-04-RC

**AMERICIUM IN QAP WATER AND AIR FILTERS -
EICHROM'S TRU RESIN**

Contact Person(s) : Anna Berne

APPLICATION

The following procedure has been applied to the preparation, separation, and analysis of spiked water and air filter samples that contain americium but not lanthanides (Berne, 1996). Lanthanides, if present, will not be removed by this method and will significantly reduce the resolution of the α -spectrograph. Combined with Procedure Pu-11-RC, this procedure allows for the sequential determination of plutonium and americium. Other researchers have applied TRU Resin methods to other matrices (Horowitz et al., 1990). The procedure is used in the EML Quality Assessment Program (QAP; Sanderson and Greenlaw, 1996).

The water and air filters are equilibrated with ^{243}Am and processed through the plutonium separation steps using ion exchange resin according to Procedure Pu-11-RC. If determination of plutonium is desired, an appropriate plutonium tracer should be added along with the ^{243}Am tracer. The eluate from the ion exchange column containing americium (and all other ions, except plutonium) is evaporated, redissolved, and loaded onto a TRU Resin extraction column. The americium (and curium, if present) is separated and purified on the column and finally stripped with dilute nitric acid stripping solution. Microprecipitation is used to prepare for α spectrometry.

SPECIAL REAGENTS

1. Americium-243 tracer solution, about 0.15 Bq g^{-1} in dispensing bottle - standardize for total disintegration rate. Measure purity on an α spectrometer.

2. TRU Resin 2 mL ion extraction columns or equivalent or can be prepared from TRU Resin, Eichrom Industries, Inc., 8205 Cass AV, Suite 107, Darien, IL 60561. Place a plug of glass wool in the bottom of a polyethylene transfer pipette (see Specification 7.7). Add slurried TRU Resin (0.5 g). Assemble immediately before use.
3. Column feed solution, 0.5M $\text{Al}(\text{NO}_3)_3$ in 2M HNO_3 - place 18.76 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in a 100-mL volumetric flask and add 2M HNO_3 to the mark. Shake to mix thoroughly.
4. 2M HNO_3 - 125 mL HNO_3 diluted to 1 L with water.
5. 1M HNO_3 - 62.5 mL HNO_3 diluted to 1 L with water.
6. 0.025M HNO_3 - 25 mL 1M HNO_3 diluted to 1 L with water.

SAMPLE PREPARATION

See Procedure Pu-01-RC, air filters or Procedure Pu-10-RC, water.

AMERICIUM DETERMINATION

1. Collect the sample and the wash effluent from Step 4, **Ion Exchange Separation**, Procedure Pu-11-RC, and evaporate almost to dryness. If necessary, sometime during the evaporation process transfer the solution to a smaller beaker. The final residue should be contained in a beaker not larger than 50 mL. Add 3 mL of 0.5M $\text{Al}(\text{NO}_3)_3$ in 2M HNO_3 to each residue and heat very gently to dissolve.
2. Prepare an ion extraction column.
3. Wash the resin with 15 mL of 2M HNO_3 , and discard the effluent.
4. Load the column with the sample solution from Step 1. Wash the beaker with 3 mL of column-feed solution and add to the column. Discard the effluent.

5. Rinse the column with 8 mL of 2M HNO₃, followed by 8 mL of 1M HNO₃, and discard the effluents.
6. Elute the americium fraction with three 3-mL aliquots of 0.025M HNO₃, and collect the eluate in a 50-mL beaker.
7. Evaporate the eluate to dryness. Convert the residue to the chloride form by adding 5 mL of HCl three times and evaporating to dryness at a low temperature.
8. Prepare the sample for α spectrometry by microprecipitation (see Procedure G-03).

DATA PROCESSING AND ANALYSIS

For α spectrometry, see Alpha Radioassay, Procedure A-01-R.

LOWER LIMIT OF DETECTION (LLD)*

Counter Efficiency	(%)	30
Counter Background	(cps)	1.6×10^{-5}
Recovery	(%)	80
Blank	(cps)	-
LLD (400 min)	(mBq)	0.5
LLD (1000 min)	(mBq)	0.3
LLD (5000 min)	(mBq)	0.1

*Reagent blanks must be analyzed with each set of samples.

REFERENCES

Berne, A.

“Use of EICrom’s TRU Resin in the Determination of Americium, Plutonium and Uranium in Air Filter and water samples.”

USDOE Report EML-575, December (1995)

Sanderson, C. G. and P. Greenlaw

“Semi-Annual Report of the Department of Energy, Office of Environmental Restoration and Waste Management, Quality Assessment Program”

USDOE Report EML-581, July (1996)

Am-05-RC

AMERICIUM IN WATER AND AIR FILTERS
(see Volume II)

Am-06-RC

AMERICIUM AND/OR PLUTONIUM IN VEGETATION

Contact Person(s) : Anna Berne

APPLICATION

This procedure is applicable to vegetation which contain americium deposited from worldwide fallout and some nuclear activities. It is most effective when used on dried finely powdered samples of vegetation.

The vegetation is either dry ashed in a ceramic crucible using a muffle furnace or wet ashed with nitric acid. Wet ashing requires considerably more time and must be carefully attended to due to the highly reactive nature of vegetation. The sample is further digested with hydrofluoric acid to dissolve silicate compounds. Plutonium is separated by ion exchange and determined by alpha spectrometry. Americium is collected with a calcium oxalate precipitation and finally isolated and purified by ion exchange. After source preparation by microprecipitation, the ^{241}Am is determined by alpha spectrometry using ^{243}Am tracer to provide recovery data.

SPECIAL APPARATUS

1. For microprecipitation, see Procedure G-03.
2. Ion-exchange columns - see Specification 7.5.

SPECIAL REAGENTS

1. Americium-243 tracer solution, about 0.15 Bq g^{-1} in a dispensing bottle-standardize for total for total disintegration rate (and/or ^{236}Pu tracer solution - a standard solution containing $\sim 0.15 \text{ Bq g}^{-1}$ in a dispensing bottle). Measure purity on an α spectrometer.
2. Anion exchange resin, Bio-Rad AG 1-X8 resin (100-200 mesh) - see Specification 7.4.
3. Anion exchange resin, Bio-Rad AG 1-X4 resin (100-200 mesh) - see Specification 7.4.
4. TRU Resin 2 mL ion extraction columns or equivalent or can be prepared from TRU Resin, Eichrom Industries, Inc., 8205 Cass AV, Suite 107, Darien, IL 60561. Place a plug of glass wool in the bottom of a polyethylene transfer pipette (see Specification 7.7). Add slurried TRU Resin (0.5 g). Assemble immediately before use.
5. 0.5M $\text{Al}(\text{NO}_3)_3$ in 2M HNO_3 - place 18.76 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in a 100-mL volumetric flask and add 2M HNO_3 to the mark. Shake to mix thoroughly.
6. 2M HNO_3 - 125 mL nitric acid diluted to 1 L with water.
7. 1M HNO_3 - 62.5 mL nitric acid diluted to 1 L with water.
8. 0.025M HNO_3 - 25 mL 1M HNO_3 diluted to 1 L with water.
9. Calcium carrier solution, 100 mg mL^{-1} - dissolve 25 g CaCO_3 in a minimal amount of concentrated HNO_3 , dilute to 100 mL.
10. Iron carrier, 100 mg mL^{-1} - slowly heat 100 g of iron powder in 500 mL of HCl until the reaction ceases. Carefully and slowly add 100 mL of HNO_3 while stirring. Cool and dilute to 1 L.
11. Oxalate wash solution - dissolve 10 g of oxalic acid to make 1 L of solution ($\sim 1\%$ solution).
12. Hydroxylamine hydrochloride, $\text{NH}_2\text{OH} \cdot \text{HCl}$.

SAMPLE PREPARATION

A. Dry ashing

1. Weigh an aliquot of < 10 g vegetation into a tared 250-mL porcelain crucible. (**Note:** After ashing, several aliquots can be combined to provide adequate sample size.) Place each crucible in a muffle furnace with the crucible cover slightly ajar. Increase the temperature of the furnace at a rate of $0.80^{\circ}\text{C min}^{-1}$ to 250°C . Maintain this temperature for 30 minutes. Increase the temperature at a rate of $10^{\circ}\text{C min}^{-1}$ to 600°C . Maintain the temperature for 960 min to completely ash sample. Cool the crucible and weigh to determine percent ash. Ash content for replicate crucibles should vary by not more than 4%. If the ash content of an individual sample is lower by more than 4%, sample loss should be assumed and that sample discarded.
2. Place a known amount (approximately same amount as ^{241}Am in the sample) of ^{243}Am tracer (and/or ^{236}Pu tracer solution) in a 400-mL beaker containing a small amount of 1:1 HNO_3 . Transfer ashed vegetation to the beaker using 1:1 HNO_3 to dissolve the ash and rinse the crucible. Transfer as many aliquots to the beaker as needed to meet the detection requirements.
3. Cover with a watch glass and reflux on a hot plate until there is no evidence of remaining organic matter, adding HNO_3 or H_2O_2 as necessary.
4. Evaporate to near dryness. Add 50 mL 1:1 HNO_3 . Filter by gravity through a Whatman No. 42 filter paper, washing with 1:1 HNO_3 into a beaker. Continue with Step 5 below.

B. Wet ashing

1. Weigh an aliquot of vegetation into an appropriate sized beaker. (For a 100-300 g sample, use a 3000-mL beaker.) Add a known amount (approximately the same amount as expected of ^{241}Am in the sample) of ^{243}Am tracer solution (and/or ^{236}Pu tracer solution).
2. Slowly add 500 mL of 1:1 HNO_3 . Control the foaming, if necessary, with the addition of a few drops of n-octyl alcohol. Cover with a watch glass and place on a

low temperature hot plate overnight, maintaining a slow reaction and stirring as necessary to break up the foam. Gradually increase the temperature of the hot plate, adding HNO_3 and maintaining refluxing until the reaction is complete as indicated by the lack of brown nitrogen oxide gas.

3. Slowly add enough HCl to equal one third the volume of HNO_3 still in the beaker. Allow the mixture to react at room temperature for 15 min, cover with a watch glass, then heat on a low temperature hot plate overnight with occasional stirring.
4. Remove the sample from the hot plate, add an equal volume of water. Allow the sample to cool to room temperature. Filter by gravity through a large Whatman No. 42 filter paper into a beaker. Wash with 1:1 HNO_3 .
5. Retain the filtrate and evaporate to near dryness. Return the residue and filter to the original beaker. Add 100 mL HNO_3 , cover with a watch glass and place on a hotplate to reflux until colorless. Change the watch glass to a ribbed watch glass and evaporate to near dryness.
6. Transfer the digested filter with the residue to a 250-mL Teflon beaker using 1:1 HNO_3 . Evaporate to dryness. Add 15 mL of HNO_3 and 15 mL of HF to the beaker and evaporate to near dryness on a medium temperature hot plate. Repeat the addition of the HF/HNO_3 and the evaporation process two or three times.
7. Add 30 mL HNO_3 and evaporate to dryness, repeat twice, rinsing the walls of the beaker with acid. Add 20 mL HNO_3 . Add 20 mL of water. Cool. Filter by gravity through a Whatman No. 42 filter paper into the beaker with the filtrate from Step 5. Rinse with 1:1 HNO_3 .
8. Evaporate filtrate to dryness. Redissolve in 30 mL 1:1 HNO_3 . Proceed to Ion Exchange Purification for Plutonium Determination, Procedure Pu-11-RC, saving the column effluents for **Americium Determination**.

AMERICIUM DETERMINATION

1. Evaporate the americium containing effluents in a beaker to incipient dryness. Redissolve in a minimum amount (20-100 mL) of 1:1 HNO_3 , dilute with four volumes of water.
2. Add 5 mL of calcium carrier solution (500 mg of calcium) and 50 g L^{-1} of oxalic acid to the sample, while stirring with a magnetic stirrer. The total volume of the sample solution can be estimated using the markings on the beaker, and the amount of oxalic acid to be added is calculated using that volume.
3. Adjust the pH of the solution to 2.0 - 2.5 with NH_4OH using pH paper as an indicator and continue to stir for 30 min. Remove the magnetic stir bar.
4. Cool and let stand until precipitate settles and solution clears. Check for completeness of precipitation using a drop of saturated $\text{H}_2\text{C}_2\text{O}_4$ solution. Aspirate as much liquid as possible without disturbing the precipitate. Transfer precipitate to a 250-mL centrifuge bottle using oxalate wash solution (see **Note 3**). Balance the bottles on a double pan balance and centrifuge for 10 min at 2000 rpm. Discard the supernate.
5. Wash the precipitate with the oxalate wash solution. Centrifuge and discard the wash. Repeat wash. Redissolve the precipitate in a minimal amount (50-70 mL) of concentrated HCl. (**Note:** Dissolution is easier if the centrifuge bottle is placed in a hot water bath and stirred with a glass stirring rod.)
6. Transfer the precipitate to the original beaker. Add ~3 volumes of water, 50 g L^{-1} of oxalic acid, and reprecipitate the oxalate with NH_4OH at a pH of 2.5-3.5 (see Step 3 above).
7. Cool the solution, aspirate, transfer to a centrifuge bottle, centrifuge, wash and redissolve the precipitate (repeat Steps 4 and 5).
8. Transfer the solution to original beaker. Add ~3 volumes of water, 50 g L^{-1} of oxalic acid, and reprecipitate the oxalate at a pH of 2.5-3.5 with NH_4OH (see Step 3).

9. Cool the solution, aspirate, transfer to a centrifuge bottle, centrifuge, wash and redissolve the precipitate in ~200 mL of concentrated HNO_3 .
10. Transfer the solution to the original beaker and heat to destroy oxalate ion. Evaporate to near dryness. Dissolve in 1:1 HNO_3 and transfer to the centrifuge bottle.
11. Add enough water to make ~1M HNO_3 . Warm the solution in a 90° hot water bath and add 200 μL iron carrier solution (20 mg iron).
12. Adjust the pH of the solution to 8-9 with NH_4OH , while stirring with a glass rod. Leave the solution in a hot water bath to digest for 20 min.
13. Cool in a cold water bath, rinse and remove the glass rod. Balance the bottles on a double pan balance and centrifuge for 40 min at 2000 rpm.
14. Aspirate the supernate and discard. Add 10 mL of concentrated HCl to dissolve the $\text{Fe}(\text{OH})_3$ pellet, four drops of 30% H_2O_2 to get rid of any Mn, followed by 100 mL of water, and heat in the water bath for 30 min to get rid of excess H_2O_2 .
15. Reprecipitate, centrifuge and redissolve. Repeat Steps 12 to 14 three times. Reprecipitate, centrifuge and redissolve. The final precipitate should be dissolved in 1:1 HNO_3 .
16. Transfer to a 250-mL beaker, evaporate to dryness, add 20 mL 1:1 HNO_3 , and evaporate to dryness again.
17. Dissolve the residue in 40 mL 1:1 HNO_3 . Cool in an ice-water bath. Add 0.6-1.0 g $\text{NH}_2\text{OH}\cdot\text{HCl}$, dissolve, and let react for 15 min. Cover with a watch glass. Heat on a low temperature hot plate to decompose unreacted $\text{NH}_2\text{OH}\cdot\text{HCl}$, then bring to gentle boil for 1-2 min. Cool and pass the solution through a 1:1 HNO_3 ion-exchange column (see **Note 1**). Collect the effluent in a 400-mL beaker. Wash with 150 mL of 1:1 HNO_3 , and collect in the beaker.
18. Evaporate the sample in the 400-mL beaker to dryness and treat several times with concentrated HCl . Dissolve the residue in 30 mL HCl . Pass this solution through a

- concentrated HCl ion exchange column (see **Note 2**). Collect the effluent in a 250-mL beaker, and wash with 100 mL of HCl. Evaporate and proceed to microprecipitation if no residue is visible. If residue remains, continue with Step 19.
19. Evaporate to dryness transferring the sample to a 50-mL beaker when volume is sufficiently diminished. Add 10-mL HNO_3 and evaporate to dryness. Add 3 mL 0.5M $\text{Al}(\text{NO}_3)_3$ in 2M HNO_3 to each residue and heat very gently to dissolve.
 20. Prepare a TRU Resin column. Wash the resin with 15 mL 2M HNO_3 , and discard the effluent.
 21. Load the sample (see Step 19) on the column. Drain to the top of the resin. Wash the beaker with 3 mL 0.5M $\text{Al}(\text{NO}_3)_3$ in 2M HNO_3 and add to the column. Discard the effluent.
 22. Rinse the column with 8 mL 2M HNO_3 , followed by 8 mL 1M HNO_3 , and discard the effluents.
 23. Elute the americium with three 3 mL aliquots of 0.025M HNO_3 into a 50-mL beaker.
 24. Evaporate eluate to dryness. Convert the residue to the chloride form by adding 3-4 mL HCl. Evaporate to dryness. Redissolve in HCl and evaporate two more times. Proceed to microprecipitation.

Notes:

1. Preparation of 1:1 HNO_3 Column. Position a plug of glass wool at the base of an 11-mm o.d. column. Transfer 15 mL of wet settled Bio-Rad AG 1-X8 resin (100-200 mesh) to the column with deionized distilled water, and allow to settle. Place a second plug of glass wool on top of the resin, and with the stopcock open allow the H_2O level to reach the top of the upper plug. Pass 150 mL (or enough so that the effluent tests free of Cl^- ion) of 1:1 HNO_3 through the resin bed in three 50-mL portions, allowing the level of each to reach the top of the upper glass wool plug.
2. Preparation of HCl Column. Position a plug of glass wool at the base of an 11-mm o.d. column. Transfer 10 mL of wet settled Bio-Rad AG 1-X4 resin (100-200 mesh)

with deionized water to the column, and allow to settle. Place a second plug of glass wool on top of the resin, and with the stopcock open allow the H₂O level to reach the top of the upper plug. Pass two 50-mL volumes of HCl through the resin bed and allow each to reach the top of the upper glass wool plug.

3. If a centrifuge is not available, centrifugation can be replaced by filtering and wet ashing the filter paper and precipitate in HNO₃.

MICROPRECIPITATION

See Microprecipitation Source Preparation for Alpha Spectrometry, Procedure G-03.

LOWER LIMIT OF DETECTION (LLD)

Counter Efficiency	(%)	25
Counter Background	(cps)	15x10 ⁻⁶
Yield	(%)	50
Blank	(cps)	-
LLD (400 min)	(mBq)	1
LLD (1000 min)	(mBq)	0.5
LLD (5000 min)	(mBq)	0.3

Iron

*Fe-01-RC**

IRON IN AQUEOUS SAMPLES - DUAL-DPM MODE LIQUID SCINTILLATION ANALYSIS

Contact Person(s) :

APPLICATION

The procedure is intended for the determination of ^{55}Fe , which decays by electron capture, in spiked aqueous samples that contain various mixed alpha, beta and gamma emitting radionuclides. Beta emitting ^{59}Fe ($E_{\text{max}} = 0.475 \text{ MeV}$) is added to the samples as the yield determinant prior to $\text{Fe}(\text{OH})_3$ scavenging. Following two anion exchange separations that remove most interferences, the samples (as FePO_4) are counted in a commercially available liquid scintillation counter that is operated in the dual-dpm mode. A single count, in a calibrated instrument, provides the quench corrected activity concentrations of ^{55}Fe in a sample based on recovered ^{59}Fe (Scarpitta and Fisenne, 1996). The procedure is adapted from ASTM (1990) and is used in the EML Quality Assessment Program (QAP, Greenlaw, 1998).

***Procedure is being revised (April 1998)**

Tritium

³H-01-RC

TRITIUM IN WATER - ACID ELECTROLYSIS
(see Volume II)

³H-02-RC

TRITIUM IN WATER - ALKALINE ELECTROLYSIS
(see Volume II)

³H-03-RC

ORGANICALLY LABELED TRITIUM - COMBUSTION PROCEDURE
(see Volume II)

³H-04-RC

TRITIUM IN WATER - LIQUID SCINTILLATION COUNTING

Contact Person(s) : Salvatore C. Scarpitta

APPLICATION

The procedure is used for the rapid determination of tritium by liquid scintillation (LS) spectrometry. It applies to all clear liquid samples and it can be completed in a short period (1 to 2 h) once efficiency curves have been established. The procedure is designed for a Tri-Carb 2250CA LS counter using Insta-Gel XF cocktail and it requires distillation of the samples so that they are free of salts and other interfering radionuclides.

The ³H spectral range or window setting is first defined. The counting efficiencies are then determined by using efficiency curves (quench curves). The efficiency curve is a plot of the counting efficiency as a function of the quench index parameter (QIP). The QIP is also known as the automatic external standardization (AES) number or the transformed spectral index of the external standard (tSIE). A sample aliquot is prepared with a measured volume of a scintillation cocktail that is then placed in a programmed LS counter for spectrum analysis.

SPECIAL APPARATUS

1. Packard Tri-Carb 2250-CA LS spectrometer
2. Low ⁴⁰K borosilicate glass scintillation vials
3. Glass distillation apparatus
4. Refrigerator

5. Tritium source - sealed 20-mL scintillation vial with cocktail.
6. Carbon-14 source - sealed 20-mL scintillation vial with cocktail.
7. Background source - sealed 20-mL scintillation vial with cocktail.
8. Glass containers - where ³H is of concern to minimize evaporative loss of water.

SPECIAL REAGENTS

1. Standardized solutions of ³H water
2. Insta-gel-XF or equivalent scintillation cocktail
3. 30% H₂O₂
4. Ethanol (95%)
5. Quenching agent - e.g., chloroform, nitromethane, carbon tetrachloride, nitric acid, etc. (**Note:** Some of the quenching agents listed are **highly** toxic and/or are carcinogens, e.g., carbon tetrachloride, and the safety of handling and disposal is the responsibility of the user.)

INTERFERENCES

1. Perform a ³H distillation if information more accurate than gross tritium is needed.
2. Reanalyze samples with excessively high count rates (e.g., > 1,000,000 counts min⁻¹) using less sample material. (**Note:** When using this procedure, the calculated ³H concentration may be higher than the actual concentration because of possible interferences from other low-energy beta emitters and the beta continuum of high-energy beta particles.)

3. Add several drops of 30% H₂O₂ to the vial to bleach the sample if quenching causes the efficiency to drop to one fourth of the highest efficiency. (**Note:** Deep color in the samples may cause severe quenching that will lower the counting efficiency.)

DETERMINATION

A. Window settings. (see Note 1)

1. Prepare unquenched ³H standards in the same geometry as the analytical samples. Set the energy regions for ³H (Region A) using the guidance found in the applicable LS counter manual.
2. Optimize the energy regions using the guidance found in the operating manual (the figure of merit is a common way to optimize the regions of interest). Follow Step 3 as an alternate.
3. Perform a spectrum analysis using the ³H standard, and visually adjust the energy range of Region A (0 to 19 keV, ³H) to maximize the count rate and minimize the energy range. A balance between the count rate and the energy range should be obtained (see **Note 2**).

Notes:

1. Determine the ³H window settings before counting the samples and backgrounds.
2. If the sample is not distilled there may be interference from low energy beta particles with the same energy as ³H, as well as from the beta continuum from high energy beta particles.

B. Efficiency as a function of quenching. (see Note)

1. Use a small volume (10-50 µL) of ³H tracer solution that has sufficient activity to give a counting error of < 1%. Prepare approximately 6-8 standards.

2. Record the tracer information (including volume, activity concentration, reference date, etc.). In order to obtain a range of quenching from high to low efficiency, pipette various volumes of the quenching agent (i.e., nitromethane) into vials, separately labeled. The following quenching agent volumes are presented as an example: 0, 0.01, 0.02, 0.03, 0.05, and 0.08 mL. (**Note: Do not** use deionized water to dilute the aqueous standard to a volume consistent with the sample set preparation.)
3. Dispense enough scintillation cocktail into each glass vial to make up the final volumes consistent with the sample set to be analyzed (e.g., 15 mL).
4. Cap and shake vigorously the scintillation vials for 10 to 20 sec. Wipe the vials clean with 95% ethanol and a paper towel. Refrigerate the vials for at least 10 min.
5. Check the stability and operational order of the LS counter before running the standards and the samples. This can be done by: counting the background, the ³H standard, and the ¹⁴C standard provided by the instrument manufacturer; using an appropriate spreadsheet program; and then comparing the count rate of these standards with previously determined standard data according to criteria currently in use.
6. Count a background sample (prepared similarly to the standards) and the ³H standards for 30 min (or until 1% counting statistics are obtained) in the regions selected on the LS counter. Record the corresponding energy regions given by the instrument.
7. Calculate the net count rate for each vial by subtracting the prepared background count rates in Region A from the measured gross count rates in Region A.
8. Determine the beta efficiency (Eff_β) for each vial in units of count per min/disintegrations per min by dividing the net activity measured in counts min⁻¹ by the calculated activity added in dpm. Also, estimate the uncertainty in the β -efficiency, ϵ -(Eff) for each vial.
9. Generate the β -efficiency curve by plotting $\text{Ln}(\text{Eff}_\beta)$ versus the QIP. (**Note:** Many LS counting systems are equipped with programs to generate efficiency curves. To use these applications, the operating manual should be referenced.)

10. Perform a least squares fit on the plot. Record the coefficients (a) and (b) for the equation $\text{Eff} = a \exp(b * \text{QIP})$ and the fitting coefficient, R. Obtain the QIP from the intercept $[\ln a]$ and the slope $[b]$.

Note: Establish efficiency curves (efficiency vs. QIP) by using artificially quenched standards. Check the efficiency curves annually and regenerate them if any major component of the instrumentation is replaced.

SAMPLE PREPARATION

1. Mark the sample identification on the appropriate scintillation vials with ink that is not removable using ethanol.
2. Pipette a known amount (e.g., 2.0 - 5.0 mL) of each sample into the appropriate scintillation vials.
3. Dispense an appropriate amount (e.g., 15 mL) of scintillation cocktail into each scintillation vial.
4. Secure the cap onto each of the scintillation vials, then shake the vials vigorously for 10 to 20 sec. Wipe each vial on the outside with a paper towel wet with ethanol to remove any fingerprints.
5. Refrigerate the samples for at least 10 min before counting. (**Note:** The samples may also need to be “dark adapted” to minimize the potential for delayed scintillations. This can be accomplished by postponing the start of counting for 10-15 min.)
6. Prepare a background sample in the same manner as the samples. A prepared background sample is one that is developed using stable compounds (e.g., dead water), and has a matrix as similar as possible to that of the samples being analyzed.

7. Count the sample for an appropriate time (e.g., 10 min) in the energy regions specified in **Determination**, Step 7. Record the QIPs given by the instrument. Return the samples to a well-ventilated area and store until disposal when the sample counts are completed.

CALCULATIONS

Perform the calculations internally with the LS software when using the DPM mode, or refer to EPA-600 4-80-032, Method 906.0 (Krieger and Whittaker, 1980).

REFERENCE

Krieger, H. L. and E. L. Whittaker

“Prescribed Procedures for Measurements of Radioactivity in Drinking Water”

U. S. Environmental Protection Agency EPA-600 4-80-032, Method 906.0, August (1980)

Lead

Pb-01-RC

**LEAD-210 IN BONE, FOOD, URINE,
FECES, BLOOD, AIR, AND WATER**

Contact Person(s) : Isabel M. Fisenne

APPLICATION

This procedure is applicable to samples of bone, food, urine, feces, blood, air, and water and is based on the solvent extraction of a lead bromide complex into Aliquat-336 (Petrov and Cover, 1965; Morse and Welford, 1971).

Lead-210 is isolated from most interferences. Its progeny ^{210}Bi is separated from ^{210}Pb , and the β activity is measured radiometrically after ingrowth.

SPECIAL APPARATUS

1. Atomic absorption (AA) spectrometer.
2. Aluminum foil - 7.2 mg cm^{-2} .
3. Rings and discs - see Specification 7.2.
4. Mylar film - see Specification 7.3.
5. Teflon filter holder.
6. Combination magnetic stirrer and hot plate.
7. Plastic scintillation phosphors - see Specification 7.9.

SPECIAL REAGENTS

1. Aliquat-336, methyltricapryl-ammonium chloride (Henkel Corporation, 2430 N. Huachuca Dr., Tucson, AZ 85745-1273), 3:7 in toluene and washed twice with an equal volume of 1.5M hydrobromic acid.
2. Hydrobromic acid 48%.
3. Hydrobromic acid 3.0M - 340 mL of 48% HBr L⁻¹ of water.
4. Hydrobromic acid 1.5M - 170 mL of 48% HBr L⁻¹ of water.
5. Hydrobromic acid 0.1M - 10 mL of 48% HBr L⁻¹ of water.
6. Toluene.
7. Standard Pb solution - 1000 µg mL⁻¹.
8. Lead carrier: 20 mg Pb mL⁻¹ - 32 g Pb(NO₃)₂ L⁻¹ in 1:19 HNO₃.
9. Bismuth carrier: 10 mg Bi mL⁻¹ - 23.2 g Bi(NO₃)₃·5 H₂O L⁻¹ in 1:19 HNO₃.

SAMPLE PREPARATION

A. Water.

1. To daily collections of 20 L of tap water add 100 mL of HNO₃ and evaporate to about 100 mL (see Note 1).
2. Add 100 mL of HNO₃ and transfer to a 400-mL beaker. Complete the destruction of organic material and evaporate to near dryness.
3. Add 50 mL of 10% HNO₃ to the beaker and warm to affect dissolution of any residue.

4. Cool the solution to room temperature and transfer the sample solution to a 100-mL volumetric flask. Bring the solution to volume with 10% HNO_3 .
5. Pipette 1 mL of sample solution into a 10-mL volumetric flask. Bring the solution to volume with 10% HNO_3 . Reserve this solution to determine the stable Pb content of the sample by AA spectrometry (see **Note 2**).
6. Return the sample solution in the 100-mL volumetric flask (Step 4) to the 400-mL beaker. Add 1 mL of Pb carrier and evaporate the solution to dryness.
7. Add 100 mL of 3M HBr to the sample beaker and warm the solution. Cool the solution to room temperature and proceed with the **Determination**.

B. Urine, blood, feces and air filters.

1. Measure 2-L of urine and transfer to a 3-L beaker. Place a measured volume of blood or 24 h fecal sample in a 1-L beaker. Place the air filter in a 600-mL beaker (see **Note 1**).
2. Destroy most of the organic material by carefully heating with HNO_3 . Hydrogen peroxide can be used to complete the oxidation of organic material (see **Note 3**).
3. Add 50-mL of 10% HNO_3 to the beaker and warm to affect dissolution of any residue.
4. Cool the solution to room temperature and transfer the sample solution to a 100-mL volumetric flask. Bring the solution to volume with 10% HNO_3 .
5. Pipette 1 mL of sample solution into a 10-mL volumetric flask. Bring the solution to volume with 10% HNO_3 . Reserve this solution to determine the stable Pb content of the sample by AA spectrometry (see **Note 2**).
6. Transfer the sample solution in the 100-mL volumetric flask (Step 4) to the 400-mL beaker. Add 1 mL of Pb carrier and evaporate the solution to dryness.

7. Add 100-mL of 3M HBr to the sample beaker and warm the solution. Cool the solution to room temperature and proceed with the **Determination**.

C. Bone (see **Note 4**)

1. Weigh 20 g of bone ash and transfer to a 400-mL beaker.
2. Dissolve the ash in about 80 mL of 3M HBr and warm to complete the dissolution.
3. Cool the solution to room temperature and transfer the sample solution to a 100-mL volumetric flask. Bring the solution to volume with 3M HBr.
4. Pipette 1 mL of sample solution into a 10-mL volumetric flask. Bring the solution to volume with 10% HNO₃. Reserve this solution to determine the stable Pb content of the sample by AA spectrometry (see **Note 2**).
5. Transfer the sample solution in the 100-mL volumetric flask (Step 3) to the 400-mL beaker and add 1 mL of Pb carrier.
6. Proceed with the **Determination**.

D. Food.

1. Depending upon food type, freeze drying should be used to remove excess water prior to wet ashing the sample (see **Note 1**).
2. Destroy most of the organic material by carefully heating with HNO₃. Hydrogen peroxide can be used to complete the oxidation of organic material (see **Note 3**).
3. Add 50 mL of 10% HNO₃ to the beaker and warm to affect dissolution of any residue.
4. Cool the solution to room temperature and transfer the sample solution to a 100-mL volumetric flask. Bring the solution to volume with 10% HNO₃.

5. Pipette 1 mL of sample solution into a 10-mL volumetric flask. Bring the solution to volume with 10% HNO₃. Reserve this solution to determine the stable Pb content of the sample by AA spectrometry (see **Note 2**).
6. Transfer the sample solution in the 100-mL volumetric flask (Step 3) to the 400-mL beaker. Add 1 mL of Pb carrier and evaporate the solution to dryness.
7. Add 100-mL of 3M HBr to the same beaker and warm the solution. Cool the solution to room temperature and proceed with the **Determination**.

Notes:

1. It is necessary to analyze reagent blanks with each batch of samples to correct the ²¹⁰Pb results.
2. The stable Pb content of some samples may be high enough to contribute a significant fraction to the total stable Pb measured by AA. This would result in an inflated estimate of the Pb carrier yield.
3. Hydrogen peroxide contains measurable and variable amounts of stable Pb and should be used sparingly.
4. It has been shown at this Laboratory that no ²¹⁰Pb loss occurs from bone dry ashed below 700°C (Fisenne, 1994). The absence of ²¹⁰Pb loss was determined for three bone types — ribs, vertebrae, and femur. It is the practice at EML to dry ash bones for ²¹⁰Pb analyses at 550°C.

DETERMINATION

1. Transfer the 3M HBr solution to a 250-mL separatory funnel containing 75 mL of Aliquat-336.
2. Shake for 30 sec. Let the phases separate and discard the aqueous (lower) phase.

3. Wash the organic phase three times with 50-mL portions of 0.1M HBr and discard all washes (lower phases).
4. Wash the organic phase twice with an equal volume of water. Transfer the washed organic phase to a suitable disposal container.
5. Combine the strip solutions in a 400-mL beaker and add 100 mL of HNO₃.
6. Wait for any reaction to subside and heat gently until the organic residue is destroyed. Evaporate the solution to ~ 10 mL.

A. First milking.

1. Transfer the sample to a 40-mL centrifuge tube with water. Add 1 mL of Bi carrier.
2. Adjust the pH of the sample to 8 with NH₄OH.
3. Stir the sample and heat in a hot water bath.
4. Cool and centrifuge the tube for 10 min. Decant and discard the supernate.
5. Dissolve the precipitate with five drops of HCl.
6. Add 40 mL of water and heat with constant stirring.
7. Cool and centrifuge for 10 min. Decant and reserve the supernate in a 250-mL beaker.
8. Repeat Steps 5-7 twice more, combining the supernates. Discard the precipitate. Record the time and date for ingrowth of ²¹⁰Bi.
9. Add 1 mL of Bi carrier and 3-5 mL of HCl to the combined supernates. Reduce the volume to <100 mL.
10. Cool, transfer to a 100-mL volumetric flask and bring to volume with 0.5N HCl.

11. Pipette 1 mL of sample into a 10-mL volumetric flask. Bring to volume with 0.5N HCl.
12. Measure the quantity of Pb in both the sample and the separated Pb fraction in the 10-mL volumetric flasks on an AA spectrometer at 283 μm . (The calibration curve should have a working range of 0-50 $\mu\text{g mL}^{-1}$.)
13. Subtract the Pb content of the dissolved sample and the reagent blank from the total Pb content determined in Step 12 to obtain the Pb carrier yield.
14. Allow 2-3 weeks for ingrowth of ^{210}Bi into the main portion of the sample (Step 10).

B. Second milking.

1. Transfer the solution from the 100-mL volumetric flask to a 250-mL beaker and evaporate to about 15 mL.
2. Transfer the sample to a 40-mL centrifuge tube and adjust the pH to 8 with NH_4OH . Centrifuge the tube for 10 min. Decant and discard the supernate.
3. Dissolve the precipitate with five drops of HCl and bring volume of sample to 30 mL with H_2O . (Record the time and date for decay of ^{210}Bi .)
4. Heat with constant stirring in a hot water bath. Cool and centrifuge the tube for 10 min. Reserve the supernate for additional ^{210}Pb analysis in a 150-mL beaker.
5. Dissolve the precipitate with five drops of HCl and dilute to 30 mL with water.
6. Heat in a hot water bath with constant stirring. Cool and centrifuge the tube for 10 min. Combine the supernate with that from Step 4.
7. Dissolve the precipitate with five drops of HCl. Stir and dilute to 30 mL with water.
8. Heat the tube in a hot water bath with constant stirring. Cool, filter with suction on a preweighed 2.4 cm Whatman No. 42 filter paper using a Teflon filter holder.

9. Wash the tube and the precipitate with water and alcohol. Dry the paper and precipitate for 30 min at 110°C in a drying oven.
10. Cool and reweigh the filter to determine weight of BiOCl precipitate.
11. Mount the filtered sample on a nylon ring and disc, covering the sample with aluminum foil (7.2 mg cm⁻²), a plastic scintillation phosphor and Mylar film.
12. Measure the ²¹⁰Bi on a low-level β-scintillation counter. (Record the time and date for decay of ²¹⁰Bi.)
13. Standardize the counter with a known amount of ²¹⁰Pb from which ²¹⁰Bi has been separated and prepared in the same way as the sample.

DATA PROCESSING AND ANALYSES

The ²¹⁰Pb activity of the sample is calculated using the following formula:

$$\text{Bq of } ^{210}\text{Pb} = \frac{R_s Y_1 Y_2 E}{GD}$$

where

R_s = net counting rate of the sample,

Y_1 = yield factor for Pb carrier,

Y_2 = yield factor for Bi carrier,

E = counter efficiency factor,

G = growth factor (growth of ²¹⁰Bi from first milking to final milking), and

D = decay factor (decay of ²¹⁰Bi from final milking to time of counting).

LOWER LIMIT OF DETECTION (LLD)

		A	B
Counter efficiency	(%)	35	-
Counter background	(cps)	0.005	-
Yield	(%)	80	80
LLD (400 min)	(Bq)	0.01	0.007
LLD (1000 min)	(Bq)	0.005	0.005

A = ^{210}Pb separation, ^{210}Bi ingrowth, ^{210}Bi separation.

B = ^{210}Bi separation only.

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Pb-02-RC

**DETERMINATION OF ^{210}Pb in BONE ASH BY
MEASUREMENT OF ^{210}Po**

Contact Person(s) : Isabel M. Fisenne

APPLICATION

The procedure has been tested for sample weights of up to 15 g of bone ash.

Lead-210 may be determined in bone samples which have been dry ashed at temperatures up to 700°C. The dry ashed bone samples should be stored for at least 2 y to allow build-up of ^{210}Po (Fisenne, 1994).

Lead, bismuth, polonium and calcium are separated from phosphate and radium as the oxalates. Lead, bismuth and polonium are separated from calcium as the sulfides. Polonium and bismuth are spontaneously deposited on a nickel disc from a weakly acid solution. The ^{210}Po is measured by alpha spectrometry and the chemical yield is determined with the alpha emitting tracer ^{209}Po .

Radium-226 is separated from the reserved oxalate supernate as the sulfate. The Ra.BaSO_4 is dissolved in alkaline EDTA and the chemical yield is determined with the gamma-emitting tracer ^{133}Ba . The ^{226}Ra is determined by the radon emanation method (see Procedure Ra-03-RC).

The total and unsupported ^{210}Pb activities are calculated from the ^{210}Po and ^{226}Ra measurements by application of the Bateman equations for the decay of this subseries of the Uranium Series (see Procedure 5.6).

SPECIAL APPARATUS

1. Nickel discs - 1.74 cm diameter by 0.06 cm thick, "commercial" pure nickel. Prior to use, degrease the disc. [**Note:** Silver or platinum discs may be used but must be cleaned and recycled. The nickel discs are discarded after measurement of the sample.]
2. Deposition cells - see Specification 7.16.
3. Mechanical stirrers.
4. Teflon stirring rods.
5. Alpha spectrometry system.
6. Radon bubblers - see Specification 7.7.
7. Polyethylene transfer pipettes - see Specification 7.11.

SPECIAL REAGENTS

1. Polonium-209 tracer solution - 1 Bq g⁻¹ of 1N HNO₃ solution.
2. Lead carrier: 20 mg Pb mL⁻¹ - 32 g Pb(NO₃)₂ L⁻¹ of 1N HNO₃.
3. Calcium carrier - solid calcium propionate. [**Note:** Calcium carrier is added only to the reagent blank. The ²¹⁰Po and ²²⁶Ra blank value must be established for each lot of calcium propionate salt prior to its use.]
4. Thioacetamide solution - 100 g CH₃CSNH₂ L⁻¹ of water.
5. Barium-133 tracer solution - 1x10⁴ Bq g⁻¹ of 1N HCl.
6. Barium carrier: 20 mg mL⁻¹ - 30.4 g BaCl₂ L⁻¹ of 1N HCl.

7. Ammonium acetate solution - 15 g NH_4OAc L^{-1} of water.
8. Acetic acid solution - 20 mL glacial HOAc L^{-1} of water.
9. Ammonium sulfate solution - 100 g $(\text{NH}_4)_2\text{SO}_4$ L^{-1} of water.
10. Aerosol OT solution - 0.1%.
11. EDTA solution - 300 g tetrasodium salt L^{-1} of water. Filter the solution through a glass fiber filter prior to use.
12. Monoethanolamine - 1:1 solution with water.

SAMPLE PREPARATION

1. Weigh 5 g of bone ash and transfer to a graduated 1500-mL beaker.
2. Add a weighed aliquot of ^{209}Po (about 0.05 g) and ^{133}Ba (about 0.1 g) tracer solutions and 1 mL of Pb carrier solution to the beaker. [**Note:** Add 2.5 g of calcium propionate to the reagent blank beaker. DO NOT ADD CALCIUM PROPIONATE TO THE BONE ASH SAMPLES.]

LEAD SEPARATION

1. Add 25 mL of HNO_3 and 1 mL of HClO_4 to the samples and reagent blank beakers. [**Note:** HClO_4 is not required for samples dry ashed at $\geq 500^\circ\text{C}$.]
2. Place the covered beakers on a medium hotplate. Swirl the beakers to dissolve the bone ash.
3. Evaporate the solution to dense HClO_4 fumes. Do not allow the sample to reach dryness.

4. Convert the sample to chloride form with five successive additions of 25 mL of HCl. Evaporate the solution to near dryness between additions.
5. Add 25 mL of HCl and swirl the beaker to dissolve most of the solids. Remove the beaker from the hotplate.
6. Dilute the solution to 1 L with water. Stir the solution with a stirring rod to dissolve any remaining solids.
7. Return the beaker to the hotplate and heat the solution for 10 min.
8. Using NH_4OH in a wash bottle, and stirring constantly, adjust the pH to about 1.5 to 2. At this point no permanent hydroxide flock should be present. Any hydroxide flock is dissolved with the addition of 6N HCL. [Note: The pH of the reagent blank is determined with pH paper.]
9. Weigh 5 g of solid oxalic acid and add to the sample with stirring. Continue heating the solution for 10 min.
10. Adjust the pH to 2.0 using NH_4OH and pH paper for both the sample and the reagent blank. Stir continuously.
11. Remove the sample from the hotplate. Remove and rinse the stirring rod with water. Allow the oxalate precipitate to settle overnight.
12. Decant the supernate into a 3-L beaker and reserve for **Radium Separation**.
13. Destroy the oxalates by evaporating with two successive 25-mL portions of HNO_3 . Do not allow the sample to reach dryness.
14. Convert the sample to the chloride form with five successive 25-mL portions of HCl.
15. Add 25 mL of HCl and swirl the beaker to dissolve most of the solids. Add a minimum amount of water to reach complete solution.

16. Remove the beaker from the hotplate and cool.
17. Transfer the solution with water to a 250-mL centrifuge bottle. Wash the beaker with water and transfer the washings to the centrifuge bottle. Stir the solution. The solution volume should be about 200 mL.
18. Place the centrifuge bottle in a 90°C hot water bath. Heat for 10 min.
19. Add 5 mL of thioacetamide solution to the sample. Stir and heat in the water bath for 1 or 2 min.
20. Remove the sample from the water bath. While stirring continuously, add NH_4OH to the sample until the black precipitate just persists.
21. Return the sample to the water bath for 1 h.
22. Remove the sample from the water bath. Remove the stirring rod and rinse with water.
23. Dry the outside of the centrifuge bottle. Place the bottle in a centrifuge cup. Tare a pair of samples on a double pan balance.
24. Place the tared samples in the centrifuge. Centrifuge the samples at 1800 rpm for 1 h.
25. Remove the samples from the centrifuge. Add 1 drop of Aerosol OT and decant the sample. Discard the supernate.
26. Add 2 mL of HCl to the sample and stir to break up the PbS precipitate. Place the sample in the water bath. Heat for 5 min.
27. Wash the walls of the bottle with 10 mL of water and heat for an additional 10 min.
28. Gravity filter the sample through a 12.5-cm diameter Whatman No. 42 paper into a prepared deposition cell.

29. Wash the centrifuge bottle with water and add the washing to the filter. Wash the filter with water. Discard the filter.
30. Place a cylindrical metal weight over the deposition cell. [**Note:** A 4-cm diameter by 4-cm height length of galvanized pipe will do.]
31. Place the weighted cell in an 80°C water bath. Lower the stirring motor with the Teflon rod in its chuck so that the rod is within 1 cm of the nickel disc.
32. Turn on the motor and stir for 4 h at maximum agitation without splashing. Add small quantities of 0.5N HCl to the cell, and water to the water bath to replace evaporative losses.
33. Turn off the motor and raise it to clear the stirring rod from the top of the cell. Remove the cell from the water bath.
34. Pour off the solution and discard. Rinse the cell successively with 0.5N HCl and water. Discard the rinsing.
35. Dismantle the cell and discard the bottle. Remove the nickel sample disc from the cap and rinse with ethanol.
36. Place the disc on a warm hotplate to dry.
37. Measure the disc in an alpha spectrometry system to determine the ^{209}Po yield and the ^{210}Po content of the sample. [**Note:** Record the deposition date so that decay corrections for the unsupported ^{210}Po can be made from separation date to measurement date.]

RADIUM SEPARATION

1. Evaporate the radium-bearing oxalate solution to dryness on a medium hotplate.

2. Remove the beaker from the hotplate and cool slightly. Add two successive 25-mL portions of HNO_3 . Heat to destroy the oxalate.
3. Convert the sample to the chloride form with five successive 25-mL portions of HCl .
4. Add 25 mL of HCl to the beaker and warm to dissolve most of the solids. Add about 50 mL of water and stir to dissolve the remaining solids.
5. Transfer the warm solution to a 250-mL centrifuge bottle. Wash the beaker with water, police and transfer the washing to the centrifuge bottle.
6. Dilute 1 mL of barium carrier to about 5 mL with water. Stir the sample thoroughly and continuously while adding the diluted carrier solution dropwise.
7. Place the centrifuge bottle in a hot water bath and warm the solution for about 5 min.
8. With constant stirring, slowly add NH_4OH until a dense white permanent hydroxide flock forms.
9. Dissolve the flock in a minimum of HCl . [**Note:** For the blank, adjust the pH from 1.5 to 2.0 using pH paper.]
10. Add 2 mL of NH_4OAc solution and 1 mL of dilute HOAc solution to the centrifuge bottle. Stir thoroughly and cool the bottle to room temperature in a water bath.
11. Add 1 mL of $(\text{NH}_4)_2\text{SO}_4$ solution to the bottle. Stir, remove the rod and rinse with water. Let the bottle stand at room temperature for 1 h.
12. Dry the outside of the centrifuge bottle. Place the bottle in a centrifuge cup. Tare a pair of samples on a double pan balance.
13. Place the tared samples in the centrifuge. Centrifuge the samples at 1800 rpm for 1 h.
14. Remove the samples from the centrifuge. Add one drop of Aerosol OT to the bottle. Carefully decant and discard the supernate.

15. Heat 5 mL of EDTA solution (300 g L^{-1}) for each sample in a hot water bath.
16. Break up the BaSO_4 precipitate with the stirring rod. Add 5 mL of warm EDTA solution and 1 mL of 1:1 monoethanolamine. Stir and heat for about 5 min.
17. Wash down the sides of the centrifuge bottle with about 10 mL of water. Continue heating the bottle for 15 min, stirring occasionally.
18. Gravity filter the solution through a 12.5-cm diameter Whatman No. 42 filter paper into a 30-mL polyethylene bottle.
19. Wash the centrifuge bottle and the filter paper with water. Discard the filter paper.
20. Dilute the sample to the same liquid level as the ^{133}Ba standard. The standard is prepared by diluting a known aliquot (about 0.1 g) of ^{133}Ba solution to 25 mL in a 30 mL polyethylene bottle.
21. Gamma count the standard and samples to determine the chemical yield of barium.
22. Transfer the solution to a radon bubbler.
23. Proceed with emanation procedure for ^{226}Ra (Ra-03-RC) to determine the radium content of the sample.

LOWER LIMIT OF DETECTION (LLD)*

		^{210}Po	^{226}Ra
Counter efficiency	(%)	30.	56.
Counter background	(cps)	$4 \times 10^{-5} \pm 0.7 \times 10^{-5}$	$2.8 \times 10^{-3} \pm 0.2 \times 10^{-3}$
Yield	(%)	85.	85.
Blank	(cps)	$3.5 \times 10^{-4} \pm 0.6 \times 10^{-4}$	$2.0 \times 10^{-2} \pm 0.8 \times 10^{-2}$
LLD (1000 min)	(mBq)	1.3	1.5
LLD (2500 min)	(mBq)	1.0	N/A

*Reagent blanks must be processed with every batch of samples.

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Env. Int. , 20, 627-632 (1994)

Polonium

Po-01-RC

POLONIUM IN WATER AND URINE

Contact Person(s) : Isabel M. Fisenne

APPLICATION

This procedure is applicable to water and urine (Hursh, 1958). Organic materials which can be converted to Cl^- solutions should also lend themselves to analysis by the procedure given. Reagent blanks must be analyzed along with the samples. [**Note:** It has been shown (Fellman et al., 1989) that urine samples must be wet ashed to release polonium from metabolically labeled organic compounds. The procedure has been modified to incorporate the destruction of organic matter.]

Polonium is quantitatively deposited on a nickel disc from a strong HCl solution. This is a very specific separation and therefore can be carried out while many other radionuclides are present in the sample.

The plated disc is α counted on a scintillation counter. It is also possible to use a ^{208}Po or ^{209}Po tracer and count on an α spectrometer to measure chemical yield and the activity of the sample.

SPECIAL APPARATUS

1. Nickel discs - made of 0.064-cm thick "commercial pure" nickel sheets. Discs are 2.2 cm in diameter with a 0.16-cm hole set 0.16 cm in from the edge. [**Note:** Coating the disc on one side with an acid resistant paint allows counting time to be cut in half.]

SAMPLE PREPARATION

A. Water.

1. To 1000 mL of tap water in a 1500-mL beaker, add 50 mL of HCl.
2. Evaporate to a volume of 20 mL and transfer to a 250-mL beaker. Add 100 mL of water and 100 mg of ascorbic acid.
3. Proceed to **Determination**.

B. Urine.

1. If the time between sample collection and analysis is much greater than 1 h, the urine samples should be preserved by adding 1 mg of sulfamic acid per mL of urine and storing in a refrigerator at 3°C.
2. Measure 100 mL of urine in a graduated cylinder and transfer to a 250-mL beaker. Rinse the graduated cylinder with 20 mL of 1:1 HNO₃ and add to the urine.
3. Evaporate the solution to near dryness and add 5 mL portions of HNO₃ to destroy organic matter.
4. Convert the sample to the Cl⁻ form by evaporating to near dryness with three successive 5-mL portions of HCl.
5. Add 20 mL of 1:1 HCl and 100 mg of ascorbic acid to the beaker.

DETERMINATION

1. Place the beaker in a constant temperature bath at 55°C.
2. Degrease a nickel disc by dipping in HNO₃, followed by dipping in HCl and rinsing in water. Repeat until the surfaces of the disc are bright and shiny.

3. Suspend the disc on a glass stirring hook in the solution and stir for 2.5 h at a speed giving maximum agitation without splashing.
4. Remove the disc, rinse the stirring rod and disc with water and let dry in air.
5. Alpha count each side of the disc. Subtract background from each count and sum the two net cps.
6. Standardize the counter with a known quantity of any α emitter on a metal disc. Natural U plated on a similar disc is a convenient standard.

LOWER LIMIT OF DETECTION (LLD)

		A	B	C
Counter Efficiency	(%)	50	50	25
Counter Background	(cps)	1.675×10^{-5}	1.67×10^{-5}	8.33×10^{-5}
Yield	(%)	70	70	70
Blank	(cps)	-	-	-
LLD (400 min)	(mBq)	0.5	0.33	1.5
LLD (1000 min)	(mBq)	0.33	0.17	1.0
LLD (5000 min)	(mBq)	0.17	0.10	0.5

A = alpha scintillation counter (both sides)

B = alpha scintillation counter (one side)

C = solid-state alpha spectrometer (one side)

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Hursh, J. B. (Editor)
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Po-02-RC

**POLONIUM IN WATER, VEGETATION,
SOIL, AND AIR FILTERS**

Contact Person(s) : Isabel M. Fisenne

APPLICATION

This procedure has been tested for water, vegetation, soil, and Dynaweb filters. Reagent blanks must be analyzed along with the samples.

Polonium is equilibrated with ^{208}Po or ^{209}Po tracer and isolated from most other elements by coprecipitation with lead sulfide. The sulfide precipitate is dissolved in weak HCl solution. Polonium is quantitatively deposited on a nickel disc. The deposition is very specific and can be carried out in the presence of other radionuclides.

The plated disc is counted on an α spectrometer to measure chemical yield and activity of the sample. The solution from the deposition may be retained and analyzed for ^{210}Pb .

SPECIAL APPARATUS

1. Nickel discs - 1.75 cm diameter x 0.06 cm thick "commercial pure" nickel. Degrease in acetone, dip in HCl and rinse with water.
2. Electrolytic cell - see Specification 7.16.
3. Teflon stirring rods.

SPECIAL REAGENTS

1. Standardized ^{208}Po or ^{209}Po tracer solution - about 2 Bq g^{-1} in a dispensing bottle.
2. Lead carrier solution: 10 mg Pb mL^{-1} - $15.98 \text{ g Pb(NO}_3)_2 \text{ L}^{-1}$ of 1:99 HNO_3 .
3. Thioacetamide solution - $100 \text{ g CH}_3\text{CSNH}_2 \text{ L}^{-1}$ of water.
4. Saturated ascorbic acid solution.

SAMPLE PREPARATION

A. Tap water.

1. Transfer 2.5 L of tap water to a 3-L beaker.
2. Add 50 mL of HNO_3 and 1 mL of Pb carrier solution. Add a weighed aliquot (30-80 mBq) of the ^{208}Po or ^{209}Po tracer solution.
3. Evaporate and add additional aliquots of tap water until a 10-L collection has been obtained. Evaporate gently to about 25 mL.
4. Transfer the solution to a 90-mL centrifuge tube with H_2O . Continue with **Determination.**

B. Vegetation.

1. Weigh 100 g of dried ($105\text{-}110^\circ\text{C}$) material into a 400-mL beaker.
2. Add 1 mL of Pb carrier solution and a weighed aliquot (30-80 mBq) of ^{208}Po or ^{209}Po tracer solution.
3. Add 100 mL of HNO_3 with magnetic stirring using a Teflon-coated bar. Digest with gentle heat and stirring for 1 h.

4. Reduce the volume of the solution to about 25 mL and transfer the solution to a 90-mL centrifuge tube with water. Continue with **Determination**.

C. Soil.

1. Weigh 1 to 5 g of soil into a 40-mL platinum dish. Add 1 mL of Pb carrier and a weighed aliquot (30-80 mBq) of ^{208}Po or ^{209}Po tracer solution.
2. Add 10 mL of HNO_3 and 10 mL of 48% HF. Heat on a medium hot plate. Repeat the additions of HNO_3 and HF until no further dissolution takes place.
3. Add 10 mL of HNO_3 and reduce the volume to about 5 mL.
4. If insoluble material remains, filter the slurry by gravity through a Whatman No. 42 filter paper into a 90-mL centrifuge tube. Wash the filter with hot water. Discard the residue. Continue with **Determination**.

C. Dynaweb filter.

1. To a 8.9 cm diameter or 1/4 of an 20.3 cm diameter Dynaweb filter in a 600-mL beaker, add 1 mL of lead carrier and a weighed aliquot (30-80 mBq) of ^{208}Po or ^{209}Po tracer solution.
2. Add 300 mL of HNO_3 and digest on a medium hot plate.
3. Evaporate to about 25 mL. If the solution is not clear, repeat the evaporation with additional HNO_3 .
4. Add about 200 mL of water to polymerize the Dynaweb material.
5. Filter with suction through a Millipore filter and wash with water. Discard the filter and polymerized Dynaweb material.
6. Transfer the filtrate back into the original beaker.

7. Reduce the volume to 25 mL. Repeat Steps 4-6 until the Dynaweb material is completely removed.
8. Transfer the solution to a 90-mL centrifuge tube. Continue with **Determination**.

DETERMINATION

1. Reduce the volume to about 5 mL in a steam bath. Add 50 mL of water.
2. Adjust the pH to 3.5-4 with NH_4OH . Add 5 mL of thioacetamide solution. Digest in a steam bath for 1 h.
3. Cool, centrifuge, and decant the supernate. Discard the supernate.
4. Dissolve the precipitate in 2 mL of HCl. Add 50 mL of water.
5. Adjust the pH to 3.5-4 with NH_4OH . Add 2 mL of thioacetamide solution. Digest in a steam bath for 1 h.
6. Cool, centrifuge, and decant the supernate. Discard the supernate.
7. Dissolve the precipitate in 1 mL of HCl. Dilute the solution to 25 mL with water.
8. Filter the solution by gravity through a Whatman No. 41 filter paper into a prepared deposition cell. Wash the filter with hot 0.5N HCl. Discard the filter.
9. Add 1 mL of saturated ascorbic acid solution to the cell.
10. Place the cell in an 80°C water bath.
11. Stir with a Teflon stirrer for 4 h at a speed giving maximum agitation without splashing. Occasional small additions of 0.5N HCl are necessary to make up for evaporation of the solution.

12. Remove the cell from the water bath and pour off the solution into a beaker. Reserve for ^{210}Pb determination if required.
13. Dismantle the cell, rinse the disc with water, then ethanol. Air dry the disc.
14. Place the disc on a warm hotplate to dry.
15. Count the disc on an α spectrometer to resolve the ^{208}Po or ^{209}Po tracer and ^{210}Po .

LOWER LIMIT OF DETECTION (LLD)

		A	B	C	D
Counter Efficiency	(%)	40	40	40	40
Counter Background	(cps)	8.33×10^{-5}	8.33×10^{-5}	8.33×10^{-5}	8.33×10^{-5}
Yield	(%)	80	75	60	60
Blank	(cps)	0.01	0.01	0.01	0.01
LLD (400 min)	(mBq)	1.5	2.0	2.0	2.0
LLD (1000 min)	(mBq)	1.0	1.3	1.3	1.3
LLD (5000 min)	(mBq)	0.4	0.6	0.6	0.6

Solid-state alpha spectrometer:

A = H_2O

B = Vegetation

C = Soil

D = Dynaweb filter

Plutonium

Pu-01-RC

PLUTONIUM IN AIR FILTERS

Contact Person(s) : Anna Berne

APPLICATION

This procedure is applicable to all types of air filters. However, if the filter is made of an organic polymer, it is advisable to first decompose the filter in a muffle furnace at 450°C overnight. Samples are then digested in concentrated HNO₃, after which the remaining residue and filter material are treated with HF.

SPECIAL APPARATUS

1. Muffle furnace.
2. Pyrex long stem fluted funnel with an inside diameter of 9.5 cm.

SPECIAL REAGENT

1. Plutonium-236 tracer - a standard solution containing ~0.15 Bq g⁻¹ in a dispensing bottle.

SAMPLE PREPARATION

1. Place the air filter in a 400-mL (or appropriate size) beaker.
2. Add a known amount (~ 0.05 Bq) of ²³⁶Pu tracer.

3. Add 150 mL of concentrated HNO_3 and 50 mL of concentrated HCl (or appropriate amounts based on air filter size), allow sample to react for about 1 h. Place the sample on a hot plate and cover with a watch glass. Heat the sample overnight on a low setting. Continue heating until the volume is ~100 mL.
4. Remove the sample from the hot plate, add 100 mL of water and let the sample cool to room temperature. Filter by gravity using a conical funnel with an 18.5 cm Whatman No. 42 filter paper. Wash with 50-75 mL of 1:1 HNO_3 . Collect the filtrate in a 250-mL beaker, evaporate the filtrate to near dryness, add ~35 mL 1:1 HNO_3 , and save. Cover the beaker with parafilm to prevent changes in the concentration of 1:1 HNO_3 .
5. Transfer the filter and residue to the original beaker and wet ash with 150-200 mL concentrated HNO_3 . Allow refluxing to occur on low heat. **Do not boil.** Evaporate to ~25-30 mL.
6. Transfer the filtered residue to a platinum dish or Teflon beaker. Add 10 mL of HF , 5 mL of HNO_3 , and evaporate to near dryness. Add 10 mL of HNO_3 and 10 mL of HF , then evaporate to near dryness again. Repeat the addition of HNO_3 and HF two more times. Wash the sides of the vessel three times with 1:1 HNO_3 , and evaporate to dryness after each addition.
7. Add 20 mL of 1:1 HNO_3 to sample.
8. Filter the sample into the beaker containing the filtrate from Step 4 by gravity filtration using a conical funnel with a 18.5 cm Whatman No. 40 or No. 42 filter paper. Wash with 1:1 HNO_3 (~ 20 mL).
9. Adjust sample volume to 100 mL with 1:1 HNO_3 .
10. Proceed to **Plutonium Purification - Ion Exchange Technique**, Procedure Pu-11-RC.

Pu-02-RC

PLUTONIUM IN SOIL SAMPLES

(see Volume II)

Pu-03-RC

PLUTONIUM IN SOIL RESIDUE - TOTAL DISSOLUTION METHOD

Contact Person(s) : Anna Berne

APPLICATION

This procedure is applicable to acid leached soils as well as unleached soils (Krey and Bogen, 1987).

The silica in the sample is removed by the formation of SiF_4 using HF. The remaining residue is fused with KF to decompose the complex silicates, followed by the addition of H_2SO_4 to distill the remaining SiF_4 . This procedure is followed by a pyrosulfate fusion, and finally, coprecipitation with BaSO_4 .

SPECIAL REAGENTS

1. Potassium fluoride.
2. Sodium sulfate.
3. Hydroxylamine hydrochloride.
4. 10% BaCl_2 solution - 10 g of BaCl_2 100 mL^{-1} of water.

SAMPLE PREPARATION

1. Using 100 mL of concentrated HNO_3 , wet ash the sample and filter the remaining sample from the leaching of the soil (Steps 2-6 of **Sample Preparation**, Procedure Pu-02-RC).

2. Evaporate the sample on a hot plate making sure the sample is completely dry.
3. Transfer the mixture to a tared plastic zip lock bag. Quantitatively remove the soil residue from the beaker. Reweigh the bag to determine the mass of the residue.
4. Break apart large aggregates by kneading the residue in the bag so that the mixture is homogeneous.
5. Weigh out 50 g of the soil residue and transfer to a 250-mL platinum crucible.
6. Add a known amount (~ 0.05 Bq or appropriate amount) of ^{236}Pu tracer.
7. Add 5 mL of 1:1 HNO_3 to wet the soil residue. Very slowly add 10 mL of concentrated HF, it may be necessary to add the HF dropwise. If excessive frothing occurs, wet the sample with 1:1 HNO_3 from a wash bottle.
8. Add an additional 10 mL of HF carefully. Heat the sample at low heat on a hot plate until no liquid remains.
9. When the sample is dry, add another 10 mL of HF. Heat the sample on a hot plate until the sample is dry.
10. Repeat Step 9 until at least a total of 100 mL of HF has been added and the sample no longer fumes. During the heating of the sample, the soil residue may move up the walls of the platinum crucible. If this occurs wash the walls with HF.
11. To insure the absence of HF, heat the crucible with a Meker burner until the crucible glows red.
12. Cool the sample and add 20 g of $\text{KF}\cdot 2\text{H}_2\text{O}$. Heat the sample on a hot plate, mixing with a Teflon stirrer.
13. Continue heating the sample until all the water has evaporated (so that no splattering occurs in the next step). It may be necessary to raise the temperature of the hot plate to assure drying.

14. Place the sample in a muffle furnace and heat at 950°C for 30 min.
15. Remove the crucible from the furnace and cool to room temperature.
16. Slowly add 35 mL of concentrated H_2SO_4 to the crucible on a hot plate at low heat. Heat the sample until the evolution of a small amount of SO_3 vapors occurs. After this step, continue heating for 5 min.
17. Cool and add 20 g of anhydrous Na_2SO_4 .
18. Place the crucible on a clay triangle mounted on a ring stand and heat the crucible gently with a Meker burner, minimizing bumping and frothing of the sample. Gradually raise the amount of heat while watching for frothing, until the molten mass is dissolved (a clear red color), at this point the temperature is $\sim 700^\circ\text{C}$. Remove the Meker burner and cool the crucible to room temperature. (**Caution:** This fusion is to be performed in a hood because SO_3 fumes are emitted.)
19. Flex the walls of the crucible to break apart the fused cake. Transfer the fused material to a 1500-mL beaker and add 200 mL of water to the crucible. Heat the crucible on a hot plate to dissolve any material in the crucible. Transfer the water wash to the 1500-mL beaker containing the fused material.
20. Perform three additional 200-mL washes of the crucible, each time transferring the solution to the 1500-mL beaker.
21. Add 100 mL of concentrated HCl , 1 g of $\text{NH}_2\text{OH}\cdot\text{HCl}$ to the 1500-mL beaker, which contains the fused material and water, and heat the solution to dissolve the fused material. Cover with a watch glass.
22. Continue to heat the solution until the boiling point is reached. Using a pipette add 5 mL of 10% BaCl_2 solution and continue boiling the sample for 5 min.
23. Cool to room temperature and filter the solution mixture by gravity through a 15-cm Whatman No. 42 filter paper using a conical funnel. Wash the beaker well with four 50-mL portions of H_2O . Transfer each H_2O wash to the funnel containing the filtered precipitate. Discard the filtrate.
24. Transfer the filter paper containing the BaSO_4 precipitate to a small platinum crucible (40 mL). Heat the crucible with a Meker burner to decompose the filter paper.

25. Add 5 g of anhydrous Na_2CO_3 to the crucible and mix the Na_2CO_3 with the BaSO_4 precipitate. Place the crucible in a muffle furnace at 850°C for 30 min.
26. Remove the crucible from the furnace, cool to room temperature, add 5 mL of water, and heat gently on a hot plate.
27. Transfer the salts and wash the solution into a 40-mL centrifuge tube using a minimum amount of H_2O to effect the transfer.
28. Centrifuge the sample and discard the supernatant.
29. Dissolve the precipitate in the centrifuge tube with 5 mL of 6M HCl. Transfer the solution mixture to a 100-mL Teflon beaker using 6M HCl. Also, wash the sides of the platinum crucible with 6M HCl to remove any remaining residue and transfer to the Teflon beaker.
30. Add 5 mL of concentrated HF, place the beaker on a hot plate and evaporate the sample to near dryness.
31. Cool, add 5 mL of 1:1 HNO_3 , and 5 mL of concentrated HF, heat on a hot plate and evaporate to near dryness.
32. Add 15 mL of 1:1 HNO_3 and evaporate to near dryness.
33. Repeat Step 32, three to five times, to remove any traces of HF.
34. Add 20 mL of 1:1 HNO_3 and heat gently for a few minutes. Remove the beaker from heat, filter mixture under reduced pressure using a 25-mm Millipore filter with a $0.45\text{-}\mu\text{m}$ pore size or by gravity filtration through a 15-cm Whatman No. 42 filter paper using a conical funnel.
35. Wash the Teflon beaker with 15 mL of 1:1 HNO_3 and transfer the wash to the filtered precipitate. Discard the precipitate. Proceed to Plutonium Purification - Ion Exchange Technique (see Procedure *Pu-11-RC*).

REFERENCE

Krey, P. W. and D. C. Bogen

"Determination of Acid Leachable and Total Plutonium in Large Samples"

J. of Radioanalytical and Nuclear Chemistry, 115, 335-355, December (1987)

Pu-04-RC

PLUTONIUM IN TISSUE
(see Volume II)

Pu-05-RC

PLUTONIUM IN TISSUE - SOLVENT EXTRACTION
(see Volume II)

Pu-06-RC

PLUTONIUM IN URINE
(see Volume II)

Pu-07-RC

PLUTONIUM IN LARGE URINE SAMPLES
(see Volume II)

Pu-08-RC

**PLUTONIUM IN VEGETATION AND TISSUE -
NITRIC/HYDROCHLORIC ACID METHOD**

(see Volume II)

Pu-09-RC

**PLUTONIUM IN VEGETATION AND TISSUE -
NITRIC/SULFURIC ACID METHOD**

(see Volume II)

Pu-10-RC

PLUTONIUM IN WATER

Contact Person(s) : Anna Berne

APPLICATION

This procedure is used for all types of water samples (i.e., sea water, lake water, tap water, etc.). If the sample contains suspended particulates, they must be removed by filtration. Large volume samples are analyzed after evaporation in an acidic medium.

The sample is heated in HNO_3 and then in 3:1 HNO_3 :HCl. The volume is then reduced to near dryness and finally the volume of the sample is adjusted with 1:1 HNO_3 . The sample is then ready to be purified by ion exchange separation (see Procedure Pu-11-RC).

SPECIAL REAGENT

1. ^{236}Pu tracer - a standard solution containing 0.2 Bq g^{-1} in a dispensing bottle. The purity of the tracer is measured by α spectrometry.

SAMPLE PREPARATION

1. Transfer 100-1000 mL of a H_2O sample to a beaker.
2. To the sample add $\sim 0.05 \text{ Bq}$ (or appropriate amount) of ^{236}Pu tracer.
3. Add an equal amount of concentrated HNO_3 , cover the beaker with a watch glass and place on a hot plate. Reflux the solution for 4-8 h.

4. Replace the watch glass with a ribbed watch glass and evaporate the solution to near dryness. When the volume is reduced to ~ 100 mL, allow the solution to cool to room temperature and transfer to an appropriate size beaker.
5. Continue evaporating the sample to near dryness. Cool, add 75 mL of concentrated HNO_3 and 25 mL of concentrated HCl . Cover with a watch glass. Allow to react for 30 min. Then place the sample on a hot plate and bring to a boil. After the solution has boiled for 30 min, reduce heat and continue heating overnight. Do not allow the sample to evaporate to dryness.
6. Remove the sample from the hot plate and add 100 mL of H_2O to the sample. Allow the sample to cool to room temperature and filter under reduced pressure using a Buchner funnel with a Whatman No. 42 filter paper.
7. Wash with 50 mL of 1:1 HNO_3 and then 50 mL of H_2O .
8. Transfer the filtrate to a 250-mL beaker, cover the beaker with a ribbed watch glass.
9. (**Note:** If the filter paper contains a moderate amount of precipitate, it must be treated with HF .) Transfer the filter paper containing the residue from the HNO_3/HCl digestion to a platinum dish. Place the platinum dish in a muffle furnace and heat at 100°C , raise the temperature by increments of 100°C every hour until a final temperature of 450°C is reached. Continue heating at this temperature overnight. Turn off the muffle furnace and let the sample in the platinum dish cool sufficiently to remove it from the furnace. Add 15 mL of 1:1 HNO_3 and 15 mL of concentrated HF . Heat the sample to near dryness.
10. Repeat Step 9 two times.
11. Add 20 mL of 1:1 HNO_3 to the sample and heat on a hot plate under a low setting until near dryness (to remove traces of HF).
12. Repeat Step 11 two times.
13. Add 20 mL of 1:1 HNO_3 to sample.

14. Using a conical funnel, filter the sample by gravity through an 18.5 cm Whatman No. 42 filter paper into a beaker containing the filtrate from Step 9. Wash well with 1:1 HNO_3 .
15. Reduce the volume of the solution to near dryness on a hot plate.
16. Adjust the volume to 100 mL by the addition of 1:1 HNO_3 .
17. Proceed to Plutonium Purification - Ion Exchange Technique, Procedure *Pu-11-RC*.

Pu-11-RC

PLUTONIUM PURIFICATION - ION EXCHANGE TECHNIQUE

Contact Person(s) : Anna Berne

APPLICATION

This procedure has been applied to the leachates derived from the plutonium sample preparation methods described in this Manual. Ion exchange chromatography is used to remove the large amounts of impurities contained in these leachates.

SPECIAL APPARATUS

Ion exchange columns - see Specifications 7.5 and 7.6.

SPECIAL REAGENTS

1. 1:1 HNO₃ - 500 mL HNO₃ diluted to 1 L.
2. Hydroxylamine hydrochloride - NH₂OH·HCl
3. 0.3M hydroxylamine hydrochloride-0.5M HNO₃ - 20.85 g of NH₂OH·HCl diluted to 1 L with 0.5M HNO₃.
4. Anion exchange resin - Bio-Rad AG 1-X8 (100-200 mesh, Cl⁻ form), see Specification 7.4

ION EXCHANGE SEPARATION

1. Cool the sample in an ice bath, add 1 g of $\text{NH}_2\text{OH}\cdot\text{HCl}$, stir, and let stand in an ice bath for 15 min. Remove the sample from the ice bath and heat to boiling on a hot plate with medium heat for 1-3 min. Cool the sample to room temperature.
2. Prepare the ion exchange resin column (see **Note**).
3. Pass the sample through the resin bed at a flow of $\sim 1 \text{ mL min}^{-1}$. Wash the beaker and the column with 30 mL 1:1 HNO_3 three times. Allow the liquid to flow until the level reaches the top of the resin bed prior to each wash. Reserve the sample and wash the effluent for ^{241}Am determination (or until yield has been determined as satisfactory).
4. Elute the plutonium with 10 mL of 0.5 M HNO_3 twice - then with 100 mL of 0.3M hydroxylamine hydrochloride - 0.5M HNO_3 into a 250-mL beaker. Discard the resin.
5. Slowly add 25-30 mL HNO_3 until effervescence begins, then place on a hot plate and evaporate the eluate to dryness.
6. Dissolve the residue in 30 mL of 1:1 HNO_3 and cool in an ice bath. Add 500-600 mg of $\text{NH}_2\text{OH}\cdot\text{HCl}$ and repeat Steps 1-3 using a small column (see Specification 7.6) for all samples.
7. Wash the resin with 100 mL of HCl (two 10-mL portions followed by two 40 mL portions). Wash the resin with two 10-mL portions, followed by one 40-mL portion 1:1 HNO_3 . Save the effluent until yield determination.
8. Repeat Steps 4 and 5. Discard the resin.
9. Convert the residue to the Cl^- form by adding 5 mL of HCl and evaporating to dryness three times at a low temperature.
10. See Procedure G-03 for microprecipitation for α spectrometry.

Note: Preparation of Columns

1. When preparing a large soil sample use a large column (Specification 7.5), otherwise use the column described in Specification 7.6.
2. Position a plug of glass wool in the base of the column so that no resin will drain out.
3. Add sufficient resin to form a resin bed of 10 cm in length. Wash the column with sufficient 1:1 HNO_3 to remove the Cl^- ion from the resin. Test the effluent with a dilute silver nitrate solution.

Pu-12-RC

PLUTONIUM AND/OR AMERICIUM IN SOIL OR SEDIMENTS

Contact Person(s) : Anna Berne

APPLICATION

This procedure is applicable to soils which contain plutonium and americium deposited from worldwide fallout and some nuclear activities. A total dissolution technique is required for some soil samples for plutonium determination.

Plutonium and americium isotopes are leached and equilibrated with ^{236}Pu and ^{243}Am tracers with nitric and hydrochloric acids from soil samples of up to 100 g in size. Plutonium is isolated and purified by ion exchange. Americium is collected with a calcium oxalate precipitation, isolated and purified by ion exchange. After source preparation by microprecipitation, the plutonium isotopes and americium are determined by alpha spectrometry.

SPECIAL APPARATUS

1. For microprecipitation, see Procedure G-03.
2. Ion-exchange columns - see Specification 7.5.

SPECIAL REAGENTS

1. Americium-243 tracer solution, $\sim 0.15 \text{ Bq g}^{-1}$ in a dispensing bottle.

2. Plutonium-236 (^{242}Pu can also be used) tracer solution, $\sim 0.20 \text{ Bq g}^{-1}$ in a dispensing bottle.
3. Bio-Rad AG 1-X8 resin (100-200 mesh) - see Specification 7.4.
4. Bio-Rad AG 1-X4 resin (100-200 mesh) - see Specification 7.4.
5. TEVA resin 2 mL ion extraction columns (Aliquat 336, methyltricapryl-ammonium chloride, Henkel Corporation, Tucson, AZ 85745-1273, on Amberchrom resin) or equivalent or can be prepared from TEVA resin, Eichrom Industries, 8205 Cass Ave. Suite 107, Darien, IL 60561) - place a plug of glass wool in the bottom of a 2 mL plastic transfer pipette (see Specification 7.7). Add slurried TEVA resin (0.5 g). Place additional glass wool on the top of the resin.
6. 2M ammonium thiocyanate in 0.1M formic acid solution - dissolve 152 g of NH_4SCN in ASTM Type 2 water, add 4.25 mL formic acid, and dilute to 1 L.
7. 1M ammonium thiocyanate in 0.1M formic acid - dissolve 76 g of NH_4SCN in ASTM Type 2 water, add 4.25 mL formic acid, and dilute to 1 L.
8. Calcium carrier solution, 100 mg mL^{-1} - dissolve 25 g CaCO_3 in a minimal amount of concentrated HNO_3 , and dilute to 100 mL.
9. Iron carrier, 100 mg mL^{-1} - slowly heat 100 g of iron powder in 500 mL of HCl until reaction ceases. Carefully and slowly add 100 mL of HNO_3 while stirring. Cool and dilute to 1 L.
10. Oxalate wash solution - dissolve 10 g of oxalic acid ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) to make 1 L of solution ($\sim 1\%$ solution).
11. Hydroxylamine hydrochloride, $\text{NH}_2\text{OH} \cdot \text{HCl}$ - solid.

SAMPLE PREPARATION

1. Weigh 1-100 g of soil into an appropriate sized beaker. Add weighed amounts of ^{243}Am and ^{236}Pu tracers.
2. Slowly add 100 mL (**Note:** volumes are based on 100 g sample and should be adjusted if sample size is smaller) of HNO_3 to the beaker. Control the foaming with the addition of a few drops of n-octyl alcohol. Stir sample with a glass stir rod to mix sample and acid. When the reaction subsides, add 30 mL of HCl , and stir. Allow the mixture to react at room temperature, rinse and remove stir rod, cover with a watch glass, then reflux on a low temperature hot plate overnight. Remove from hot plate and cool.
3. Dilute the solution in the beaker with water to 1:1 HNO_3 and filter the solution with vacuum through 9 or 11 cm Whatman No. 42 filter paper on a Büchner funnel into a 1 L flask. Wash with 1:1 HNO_3 . Retain the filtrate in a 2-L beaker, evaporate the filtrate until salting out begins to occur. Return the residue and filter to the original beaker using HNO_3 to complete the transfer.
4. Add HNO_3 to the beaker to bring the volume added to 100 mL. Stir with a glass rod to mix sample and acid. Cover with a watch glass and heat until filter is wet ashed. Remove from the hotplate and cool. Add 30 mL of HCl to the beaker, cover with the watch glass, and heat on a low temperature hot plate for about 3 h with occasional stirring. Remove the beaker from the hot plate, and cool.
5. Repeat Step 3; dilute, filter and wash. Combine the filtrates. Return the residue and filter to the original beaker.
6. Repeat Step 4; wet ash filter and leach sample.
7. Repeat Step 3; dilute, filter and wash. Combine the three filtrates in a beaker. Discard the residue and filter paper.
8. Heat the filtrate with repeated 50-mL additions of HNO_3 , covering the sample with a watch glass and letting the sample reflux until all organic matter is decomposed. Evaporate the solution to incipient dryness. Redissolve in 50-200 mL of 1:1 HNO_3 .

If the solution is not clear, proceed to Step 9, otherwise go to **Plutonium Determination**.

9. If any siliceous matter is present, filter into a flask by gravity through a Whatman No. 42 filter paper. Wash the residue with 1:1 HNO_3 , and reserve the filtrate.
10. Transfer the filter paper with the residue to the original beaker and wet ash the paper with 100 mL of HNO_3 . Repeat wet ashing two or three times, then transfer the residue in the beaker into a 250-mL Teflon beaker, using 1:1 HNO_3 . Evaporate to dryness.
11. Add 5-25 mL of HF and 5-25 mL of HNO_3 to the beaker and evaporate on a medium temperature hot plate. Repeat the addition of the HF/ HNO_3 and the evaporation process two or three times. Rinse the walls of the Teflon beaker with 1:1 HNO_3 and evaporate, and repeat. Evaporate to dryness. Dissolve with 1:1 HNO_3 and evaporate to dryness.
12. Dissolve the residue in 1:1 HNO_3 and filter by gravity through a Whatman No. 42 filter paper. Add the filtrate to the solution from Step 9. Discard the filter and any residue. Heat the combined solution to incipient dryness. Redissolve in 50-200 mL 1:1 HNO_3 .

PLUTONIUM DETERMINATION

Proceed to Plutonium Purification Ion Exchange Technique Procedure *Pu-11-RC*. Save the column effluents for **Americium Determination**.

AMERICIUM DETERMINATION

1. Evaporate the americium effluents to incipient dryness. Redissolve in a minimum amount of 1:1 HNO_3 , dilute with four volumes of water.

2. Add 5 mL of calcium carrier solution (500 mg of calcium) and 50 g L⁻¹ of oxalic acid to the sample while stirring with a magnetic stirrer. (**Note:** The total volume of the sample solution can be estimated using the markings on the beaker, and the amount of oxalic acid to be added is calculated using that volume.)
3. Adjust the pH of the solution to 2.0-2.5 with NH₄OH using pH paper as an indicator and continue to stir for 30 min. Remove the magnetic stir bar.
4. Cool the sample and let it stand until precipitate settles and solution clears (for more than 6 h or overnight). Check for completeness of precipitation using a drop of saturated H₂C₂O₄ solution. Aspirate (or decant), using a disposable transfer pipette and suction, as much liquid as possible without disturbing the precipitate. Transfer the precipitate to a 250-mL centrifuge bottle using oxalate wash solution (see **Note 1**). Balance the bottles on a double pan balance and centrifuge for 10 min at 2000 rpm. Decant and discard the supernate.
5. Break up the precipitate with a stirring rod and wash the precipitate with the oxalate wash solution. Centrifuge, decant and discard the wash. Repeat wash. Redissolve the precipitate in a minimal amount (50-70 mL) of concentrated HCl (the final precipitate should be redissolved in ~200 mL of HNO₃, then proceed to Step 8 below). (**Note:** Dissolution is easier if the centrifuge bottle is placed in a hot water bath and stirred with a glass rod).
6. Transfer the dissolved precipitate to the original 600-mL beaker. Add enough water to make ~ 1M solution. Add 50 g L⁻¹ of oxalic acid.
7. Repeat Steps 3 through 6 until supernate is colorless.
8. Transfer the dissolved precipitate to the original beaker and heat to destroy the oxalate ion. Evaporate to near dryness. Dissolve in a minimum of 1:1 HNO₃. Transfer to centrifuge bottle using water to complete the transfer.
9. Add enough water to make ~1M HNO₃. Warm the solution in a 90° hot water bath and add 0.2 mL iron carrier solution (20 mg iron).

10. With the centrifuge bottle in the hot water bath adjacent to a hood, adjust the pH of the solution to 8-9 with NH_4OH while stirring with a glass rod. Allow the solution to digest in a hot water bath for 20 min.
11. Cool in a cold water bath, rinse, and remove the glass rod. Balance the bottles on a double pan balance and centrifuge for 40 min at 2000 rpm.
12. Decant (or aspirate) and discard the supernate. Add 10 mL concentrated HCl to dissolve the $\text{Fe}(\text{OH})_3$ pellet. Add four drops 30% H_2O_2 to oxidize any Mn present, followed by 100 mL of water and heat in the water bath for 30 min to get rid of excess H_2O_2 .
13. Repeat Steps 10 to 12 three times. Reprecipitate, centrifuge and redissolve. The final precipitate should be redissolved in HNO_3 .
14. Transfer to a 250-mL beaker, evaporate to dryness, add 20 mL HNO_3 , and evaporate to dryness again.
15. Dissolve the wet-ashed residue in 40 mL 1:1 HNO_3 . Cool in an ice-water bath. Add 0.6-1.0 g $\text{NH}_2\text{OH} \cdot \text{HCl}$, dissolve, and let react for 15 min. Cover with a watch glass. Heat on a low temperature hot plate to decompose unreacted $\text{NH}_2\text{OH} \cdot \text{HCl}$, then bring to gentle boil for 1-2 min. Cool and pass the solution through a 1:1 HNO_3 ion-exchange column (see **Note 2**). Collect the effluent in a 400-mL beaker. Wash the column with 150 mL of 1:1 HNO_3 and collect in the beaker.
16. Evaporate the sample in the 400-mL beaker to dryness. Convert to HCl by adding 20-30 mL of HCl at a time, heat to almost dryness, and repeat the HCl addition and evaporation at least three times. Evaporate again and dissolve the final residue in 30 mL of HCl . Pass this solution through a 12N HCl ion exchange column (see **Note 3**). Collect the effluent in a 250-mL beaker. Wash the column with 100 mL of HCl and collect in the 250-mL beaker.
17. Evaporate to dryness. Dissolve the residue in 10 mL 2M NH_4SCN in 0.1M formic acid.

18. Prepare a TEVA column. Equilibrate the resin by adding 3-4 mL 2M NH_4SCN in 0.1M formic acid. Drain to the top of the resin.
19. Transfer the sample to the column. Drain to the top of the resin.
20. Wash the column with 10 mL 1M NH_4SCN in 0.1M formic acid. Discard wash.
21. Elute the americium with 15 mL 2M HCl into a clean 100-mL beaker.
22. Add approximately 10 mL aqua regia to the sample. Gently decompose the thiocyanate solution under a heat lamp. Allow the solution to develop a purple color which will slowly disappear.
23. Heat the sample on a hot plate to near dryness. Dissolve the residue in 3 to 4 mL HNO_3 . Evaporate to dryness. Redissolve in HNO_3 and evaporate two more times.
24. Convert to HCl by addition of 3-4 mL HCl . Evaporate to dryness. Redissolve in HCl and evaporate two more times. Proceed to microprecipitation.

Notes:

1. If a centrifuge is not available, centrifugation can be replaced by filtering and wet ashing filter paper and precipitate in HNO_3 .
2. Preparation of 1:1 HNO_3 column. Position a plug of glass wool at the base of an 11-mm o.d. column. Transfer with ASTM Type 2 water, 15 mL of wet settled Bio-Rad AG 1-X8 resin (100-200 mesh) to the column and allow it to settle. Place a second plug of glass wool on top of the resin, and with the stopcock open allow the water level to reach the top of the upper plug. Pass 150 mL (or enough so that the effluent tests free of Cl^- ion) of 1:1 HNO_3 through the resin bed in three 50-mL portions, allowing the level of each to reach the top of the upper glass wool plug.
3. Preparation of HCl column. Position a plug of glass wool at the base of an 11-mm o.d. column. Transfer with ASTM Type 2 water, 10 mL of wet settled Bio-Rad AG 1-X4 resin (100-200 mesh) to the column and allow it to settle. Place a second plug of glass wool on top of the resin and with the stopcock open allow the water level to reach the top of the upper plug. Pass two 50-mL volumes of HCl through the resin bed and allow each to reach the top of the upper glass wool plug.

MICROPRECIPITATION

See Microprecipitation Source Preparation for Alpha Spectrometry, Procedure G-03.

AMERICIUM LOWER LIMIT OF DETECTION (LLD)

Counter Efficiency	(%)	25
Counter Background	(cps)	15×10^{-6}
Yield	(%)	50
Blank	(cps)	-
LLD (400 min)	(mBq)	1
LLD (1000 min)	(mBq)	0.5
LLD (5000 min)	(mBq)	0.3

PLUTONIUM LOWER LIMIT OF DETECTION (LLD)

Counter Efficiency	(%)	25
Counter Background	(cps)	2×10^{-5}
Yield	(%)	75
Blank	(cps)	-
LLD (400 min)	(mBq)	1
LLD (1000 min)	(mBq)	0.5
LLD (5000 min)	(mBq)	0.2

Radium

Ra-01-RC

RADIUM-226 IN BONE ASH

Contact Person(s) : Isabel M. Fisenne

APPLICATION

This procedure is applicable to bone ash only and has been adapted from Hallden et al. (1963).

The separated sample is measured by radon emanation. Only ^{226}Ra yields a radon progeny with suitable characteristics, so the method is specific. Most of the calcium, the alkali metals and phosphates are separated by coprecipitation of the radium as sulfate with barium carrier in a buffered solution. Further purification is obtained by repeating this step in the presence of undissolved BaSO_4 . The sulfate precipitate is dissolved in alkaline EDTA to prepare the emanating solution. The chemical yield of barium is determined with the γ -emitting tracer ^{133}Ba .

SPECIAL APPARATUS

Radon bubblers - see Specification 7.7.

SPECIAL REAGENTS

1. Barium-133 tracer solution - about 50 counts sec^{-1} per 0.1-g aliquot, prepared in 1:99 HCl.
2. Barium carrier solution (20 mg mL^{-1}) - 30.4 g $\text{BaCl}_2 \text{ L}^{-1}$ of 1:99 HCl.

3. Ammonium acetate solution - 15 g $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ (NH_4OAc) L^{-1} of water.
4. Acetic acid solution - 20 mL glacial $\text{CH}_3\text{CO}_2\text{H}$ (HOAc) L^{-1} of water.
5. Ammonium sulfate solution - 100 g $(\text{NH}_4)_2\text{SO}_4$ L^{-1} of water.
6. Aerosol OT solution - 0.1%.
7. EDTA solution - 300 g tetrasodium salt of EDTA L^{-1} of water.
8. EDTA wash solution - 1:9 dilution of EDTA solution.
9. Monoethanolamine - 1:1 (v/v) with water.

DETERMINATION

1. Weigh 10 g of bone ash into a 90-mL glass or 100-mL polycarbonate centrifuge tube. Add a weighed aliquot (about 0.1 g) of ^{133}Ba tracer solution, and 1 mL of barium carrier solution.
2. Add 20 mL of HCl (slowly at first to prevent foaming). Stir and warm in an 85°C water bath for about 5 min.
3. Add 10 mL of water. Add NH_4OH until a dense white permanent hydroxide flock forms (about 8-10 mL).
4. Dissolve the flock in HCl (about 4 mL is required).
5. Add 2 mL of NH_4OAc solution and 1 mL of HOAc solution. Cool in a water bath to room temperature.
6. Add 1 mL of $(\text{NH}_4)_2\text{SO}_4$ solution. Stir and let stand for 0.5 h.
7. Centrifuge at 2000 rpm for 1 h. Add one drop of 0.1% Aerosol OT. Decant carefully and discard the supernate.

8. Add 5 mL of HCl and warm in an 85°C water bath for 5 min. (Most of the BaSO₄ remains as a precipitate.)
9. Add 10 mL of water and then add NH₄OH until a permanent flock forms.
10. Dissolve the flock in HCl.
11. Add 2 mL of NH₄OAc solution and 1 mL of HOAc solution. Cool in a water bath to room temperature.
12. Add 1 mL of (NH₄)₂SO₄ solution. Stir and let stand for 0.5 h.
13. Centrifuge at 2000 rpm for 1 h. Add one drop of 0.1% Aerosol OT. Decant carefully and discard the supernate.
14. Heat a solution of EDTA (300 g L⁻¹) and an EDTA wash solution (30 g L⁻¹) in an 85°C water bath.
15. Break up the BaSO₄ precipitate with a stirring rod. Add 1 mL of 1:1 mono-ethanolamine and 5 mL of the hot EDTA solution and stir. Let stand for 5 min.
16. Wash down the sides of the tube with about 10 mL of the hot EDTA wash solution. Let the tube remain in the water bath for 15 min, stirring occasionally.
17. Gravity filter the hot solution through a 12.5 cm Whatman No. 41 filter paper into a 30 mL polyethylene bottle.
18. Wash the centrifuge tube and the filter paper with hot EDTA wash solution. Discard the paper and residue.
19. Dilute the sample to the same liquid level as the ¹³³Ba standard. The standard prepared by diluting a known aliquot (about 0.1 g) of ¹³³Ba solution to 25 mL in a 30 mL polyethylene bottle. Gamma count on a flat crystal to determine the chemical yield of barium.
20. Transfer the sample solution to a ²²²Rn bubbler.

21. De-emanate ^{222}Rn by bubbling with forming gas for about 10 min at $100\text{ cm}^3\text{ min}^{-1}$ as described in Radium - Emanation Procedure (see Ra-02-RC). Record the time as the starting time for ^{222}Rn buildup. Continue the analysis using the emanation technique.

LOWER LIMIT OF DETECTION (LLD)

Counter Efficiency	(%)	57.5
Counter Background	(cps)	0.0028
Yield	(%)	90
Blank	(cps)	0.0012
LLD (400 min)	(mBq)	3.3
LLD (1000 min)	(mBq)	1.7

*Reagent blanks must be analyzed with each set of samples.

REFERENCE

Hallden, N. A., I. M. Fisenne and J. H. Harley
"The Determination of Radium-226 in Human Bone"
Talanta, 10, 1223-1227 (1963)

Ra-02-RC

RADIUM-226 - EMANATION PROCEDURE

Contact Person(s) : Isabel M. Fisenne

APPLICATION

This procedure is specific and may be applied to almost any matrix which can be converted to a homogeneous solution.

Radium-226 in solution can be determined by de-emanating its ^{222}Rn into an ionization chamber or scintillation cell for measurement. The ^{222}Rn can be de-emanated by bubbling an inert gas through the solution, either after equilibrium has been established or after any known time period. Two half-lives, 7.65 days for example, give 75% of the maximum buildup.

SPECIAL APPARATUS

1. Radon measuring equipment are described in Radon-222 in Air and Breath Samples, Procedure Rn-01-RC, and in Fisenne and Keller (1985).
2. Radon bubblers - see Specification 7.7.

SAMPLE PREPARATION

1. The sample with barium carrier should be in homogeneous solution in a volume of 15-25 mL. The solution should be acidic with perchloric acid, neutral or in basic EDTA solution. Hydrochloric acid, NH_3 or other volatile materials must be absent.

2. Detailed preparation procedures for separation of Ra from sample matrices are presented in other radium procedures in this Manual.
3. Almost all types of samples require simultaneous analysis of reagent blanks, since radium appears in many chemical compounds. Using distilled or organic reagents reduces possible contamination.

DETERMINATION

1. Transfer the sample solution to a ^{222}Rn bubbler.
2. Clamp the bubbler in place to the ^{222}Rn system.
3. Open the forming gas (85% N_2 , 15% H_2) tank valve and adjust the line pressure to 70 kPa (10 psi) gauge.
4. Bleed the gas line, the rotometer, and 9.5 mm diameter rubber tubing.
5. Adjust the flow through the rotometer to a rate of $20 \text{ cm}^3 \text{ min}^{-1}$.
6. Open both stopcocks on the ^{222}Rn bubbler.
7. Attach the rubber tubing on the exit of the rotometer to the inlet of the ^{222}Rn bubbler. Adjust the forming gas flow rate through the bubbler to $100 \text{ cm}^3 \text{ min}^{-1}$.
8. Flush the ^{222}Rn from the solution (de-emanate) for 10 min.
9. Close both stopcocks simultaneously. Record the date and time as the beginning of the ^{222}Rn build-up period.
10. Shut off the forming gas and remove the rubber tubing from the bubbler.
11. Place the ^{222}Rn bubbler in a refrigerator for a suitable build-up period, usually 1 week.
12. To emanate ^{222}Rn into a pulse ionization chamber, repeat Steps 2-4.

13. Attach the rubber tubing from the rotometer to the inlet of the measurement system.
14. Open the valve to the ionization chamber and close the vacuum valves. Partially fill the chamber with forming gas to a pressure of -2.7 (-50 cm of Hg) gauge. Close the chamber valve and system entry valve. Open the vacuum valves and detach the rubber tubing from the measurement system.
15. Attach a small drying tube containing about 5 g of a color indicating drying agent and 4 cm lengths of 9.5 mm diameter rubber tubing at both ends to the outlet of the bubbler and the inlet of the measurement system.
16. Open the system entry valve to evacuate the drying tube for 3 min.
17. Adjust the forming gas flow rate to $20 \text{ cm}^3 \text{ min}^{-1}$ and attach the tubing outlet of the rotometer to the inlet of the bubbler.
18. Close the vacuum valves and open the ionization chamber valve.
19. Open the outlet stopcock of the bubbler and allow the bubbling to subside. Record the date and time as the end of the ^{222}Rn build-up period.
20. Carefully open the bubbler inlet stopcock and adjust the forming gas flow through the bubbler to about $100 \text{ cm}^3 \text{ min}^{-1}$.
21. When the system gauge indicates that atmospheric pressure has been reached, close both bubbler stopcocks simultaneously. Close the chamber, system entry and forming gas valves. Open the vacuum valves.
22. Remove the bubbler and drying tube from the system. Record the date and time of the end of the emanation as the beginning of the next ^{222}Rn build-up period.
23. Turn on the ionization chamber high voltage. A red LED will light when the chamber is at or above atmospheric pressure.
24. Measure the sample for at least 17 h.

Notes for Proper Operation:

1. If the Teflon stopcocks of the bubbler are snug fitting, it is not necessary to grease them. If they do leak, however, a silicone stopcock grease may be used.
2. The glass-to-glass ground joint at the top of the bubbler should also be lightly greased with silicone.
3. During the de-emanation, the gas bubbling should be started slowly to prevent popping of the bubbler top or stopcocks.
4. A better transfer of ^{222}Rn from acid or neutral solutions is obtained if the bubbler is first chilled in a refrigerator. This apparently reduces the bubble size and improves the transfer efficiency. For samples dissolved in alkaline EDTA solution, a drop of octyl alcohol is added to reduce foaming.

STANDARDIZATION

The chambers are standardized by de-emanating aliquots of a National Institute of Standards and Technology SRM ^{226}Ra solution contained in ^{222}Rn bubblers.

DATA PROCESSING AND ANALYSES

1. For routine work, discard the first 5 h of counting data (equilibrium for ^{222}Rn and progeny).
2. Determine the total count over the remaining counting period.
3. Calculate the net counts per hour per sample by determining the total sample counts per hour and subtracting the background counts per hour.
4. Divide the net counts per hour by the chamber standardization value of net counts per hour per Bq of ^{222}Rn .
5. Using the midpoint of the counting interval as the time of counting, extrapolate the value obtained to the time noted for the end of ^{222}Rn buildup. Figure 1 may be used for this calculation. This correction is only a few percent. The decay during the counting period is small and is not corrected for.

6. Correct the ^{222}Rn measurement at the end of buildup for the fractional buildup. The figure in Procedure Rn-01-RC may be used to obtain the build-up factor.
7. Subtract the value obtained by carrying a blank determination through the full procedure.
8. Samples are measured twice and the mean and standard deviation of the duplicate emanation results are reported.
9. A computational data sheet is attached for handling routine calculations on a step-by-step basis.

LOWER LIMIT OF DETECTION (LLD)*

Counter Efficiency	(%)	57.5
Counter Background	(cps)	0.0028
Yield	(%)	90
Blank	(cps)	0.0012
LLD (400 min)	(mBq)	3.3
LLD (1000 min)	(mBq)	1.7

*Reagent blank must be analyzed with each set of samples.

REFERENCE

Fisenne, I. M. and H. W. Keller

"The EML Pulse Ionization Chamber Systems for the Measurement of Radon-222"

USDOE Report EML-437, March (1985)

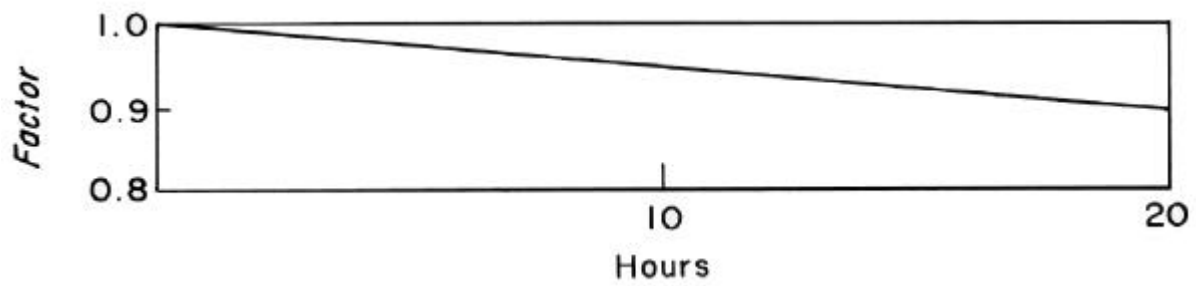


Figure 1. Correction factor from midpoint to the counting interval to the start of radon measurements interval.

Date _____

Sample Number

		Operation						
1	Chamber number	-						
	BACKGROUND							
2	Total count	-						
3	Count interval (h)	-						
4	Background (cph)	2/3						
	STANDARDIZATION							
5	Chamber factor cph Bq ⁻¹	-						
	SAMPLE COUNT							
6	Total count	-						
7	Count interval (h)	-						
8	Sample at count time (cph)	6/7						
	CORRECTIONS							
9	Time for midpoint of count	-						
10	Time for end of buildup	-						
11	Difference (days)	9-10						
12	Factor (from graph)	-						
13	Sample at end of buildup	8/12						

Date _____

Sample Number

		Operation						
14	Time for start of buildup	-						
15	Time for end of buildup	10						
16	Difference	15-14						
17	Factor (from graph)	-						
18	Sample with full buildup	13/17						
19	Bq in sample	18/5						
20	Bq in blank*							
21	Net Bq in sample	19-20						

*This sheet is suitable for calculating the blank value.

Ra-03-RC

**RADIUM-226 IN SOIL, VEGETATION ASH,
AND ION EXCHANGE RESIN**

Contact Person(s) : Isabel M. Fisenne

APPLICATION

This procedure is applicable to 5 g samples of soil and 10 g of vegetation ash or to ion exchange resin from sampling columns.

Soil, vegetation ash or ion exchange resin are prepared for ^{222}Rn emanation measurement. The sample is pretreated with HNO_3 -HF, fused with KF and transposed to pyrosulfate (Sill, 1961). The cake is dissolved in dilute HCl. RaBaSO_4 is precipitated, filtered, and dissolved in alkaline EDTA. The chemical yield is determined with the γ -emitting tracer ^{133}Ba .

SPECIAL APPARATUS

1. Radon bubblers - see Specification 7.7.
2. 100 mL platinum dishes or 250 mL platinum crucibles.
3. Millipore filter setup - 47 mm diameter.
4. Millipore filters - 47 mm diameter, 0.45 μm pore size.

SPECIAL REAGENTS

1. Barium-133 tracer solution - about 50 cps per 0.1-g aliquot, prepared in 1:99 HCl.
2. Barium carrier solution (20 mg mL^{-1}) - $30.4 \text{ g BaCl}_2 \text{ L}^{-1}$ in 1:99 HCl.
3. EDTA solution - 300 g tetrasodium salt of EDTA L^{-1} of water.
4. Triethanolamine - 1:1 in water.

SAMPLE PREPARATION

A. Soil and vegetation.

1. Weigh 5 g of soil or 10 g of vegetation ash into a 100-mL platinum dish. Add a weighed aliquot (about 0.1 g) of ^{133}Ba tracer solution and 1 mL of Ba carrier solution.
2. Slowly add 10 mL of HNO_3 and 10 mL of HF to the sample and evaporate on a hot plate to near dryness.
3. Continue the analysis as described below.

B. Ion exchange resin.

1. Transfer the resin and paper pulp from the collection column to a 250-mL platinum crucible. Dry under a heat lamp and ash at 500°C in a muffle furnace for 48 h.
2. To the cooled crucible, add a weighed aliquot (about 0.1 g) of ^{133}Ba tracer solution and 1 mL of barium carrier solution.
3. Continue the analysis as described below.

DETERMINATION

1. Weigh out 15 g of KF and add to the sample. Press the KF into the sample with a plastic spatula.

Caution - wear rubber gloves and safety glasses during Steps 2-5.

2. Fuse the sample over an air fed Meker burner, gradually increasing the temperature until a clear melt is obtained. Cool the melt.
3. Using a burette, slowly add 17.5 mL of H_2SO_4 to the melt. Heat the dish on a hot plate until a clear melt accompanied by dense fumes is obtained. Cool the melt.
4. Weigh out 10 g of Na_2SO_4 , add to the dish and fuse over the Meker burner until a clear melt accompanied by dense fumes is obtained. Cool the melt.
5. Transfer the cake to a 600 mL beaker containing 350 mL of hot water and 25 mL of HCl. Stir the solution to dissolve the cake. Cool for 1 h.
6. Filter the precipitate onto a 47 mm diameter, 0.45 μm pore size Millipore filter into a 1 L sidearm flask, police the beaker, and wash with water. Add the washing to the funnel. Discard the filtrate.
7. Using a strong stream of water from a wash bottle, transfer the precipitate from the filter into a 150 mL beaker. Discard the filter.
8. Add 5 mL of EDTA solution and 1 mL of 1:1 triethanolamine to the beaker. Heat on a warm hot plate for about 15 min, stirring occasionally. Reduce the sample volume to ~15 mL.
9. Gravity filter the warm solution through a Whatman No. 41 filter paper into a 30-mL polyethylene bottle.
10. Wash the beaker dish and filter with hot water. Discard the filter.

11. Dilute the sample to the same liquid level as a known aliquot (about 0.1 g) of the ^{133}Ba tracer solution and dilute to 25 mL in a 30 mL polyethylene bottle.
12. Gamma count the samples and standard to determine the chemical yield of barium.
13. Transfer the sample to a ^{222}Rn bubbler with water.
14. De-emanate ^{222}Rn by bubbling with forming gas for about 10 min at 100 mL min^{-1} as described in $^{226}\text{Radium}$ - Emanation Procedure (see Ra-02-RC). Record the time as the starting time for ^{222}Rn buildup. Continue the analysis by the emanation technique.

LOWER LIMIT OF DETECTION (LLD)*

Counter Efficiency	(%)	57.5
Counter Background	(cps)	0.0028
Yield	(%)	90
Blank	(cps)	0.0020
LLD (400 min)	(mBq)	3.3
LLD (1000 min)	(mBq)	1.7

*Reagent blanks must be analyzed with each set of samples.

REFERENCE

Sill, C. W.

"Decomposition of Refractory Silicates in Ultramicro Analysis"

Anal. Chem., 33, 1684 (1961)

Ra-04-RC

RADIUM-226 IN TAP WATER, URINE, AND FECES

Contact Person(s) : Isabel M. Fisenne

APPLICATION

The procedure presented has been applied to tap water, ashed urine, and feces samples. Only ^{226}Ra yields ^{222}Rn progeny that has suitable characteristics for detection by an emanation technique; therefore, the procedure is specific.

After sample preparation, radium is isolated from most other elements by coprecipitation with barium sulfate. Further purification is obtained by the removal of silica with HF and reprecipitation of the sulfate. The sulfate precipitate is dissolved in alkaline EDTA to prepare the emanating solution. The chemical yield of barium is determined with the γ -emitting tracer ^{133}Ba .

SPECIAL APPARATUS

Radon bubblers - see Specification 7.7.

SPECIAL REAGENT

1. Barium carrier solution - 20 mg mL^{-1} - 30.4 g $\text{BaCl}_2 \text{ L}^{-1}$ in 1:99 HCl.
2. Ammonium sulfate solution - 100 g $(\text{NH}_4)_2\text{SO}_4 \text{ L}^{-1}$ in water.
3. Aerosol OT solution - 0.1%.

4. EDTA solution - 300 g tetrasodium salt of EDTA L⁻¹ in water.
5. EDTA wash solution - 1:9 dilution of EDTA solution.
6. Ammonium acetate solution - 15 g L⁻¹ in water.
7. Acetic acid solution - 20 mL glacial acetic L⁻¹ in water.
8. Triethanolamine - 1:1 in water.

SAMPLE PREPARATION

A. Tap water.

1. Transfer two 0.5-L of tap water to a 3 L beaker.
2. Add 25 mL of HCl and 1 mL of barium carrier solution. Add a weighed aliquot (about 0.1 g) of the ¹³³Ba tracer solution.
3. Evaporate and add an additional two 0.5-L aliquots of tap water until a 10-L collection has been obtained. Evaporate gently to about 100 mL.
4. Transfer to a 400-mL beaker with water, policing the sides of the 3-L beaker thoroughly. Evaporate gently to about 100-mL.
5. Adjust the pH to 4 with 1:1 NH₄OH and proceed with **Determination**.

B. Urine.

1. Weigh an aliquot of ¹³³Ba tracer solution (about 0.1 g) into a 2-L beaker containing a small amount of water and 1 mL of barium carrier solution.
2. Add 1500 mL of urine, then 100 mL of HNO₃ and evaporate to about 1-L.
3. Slowly add 100-mL of HNO₃.

4. Repeat the evaporation and addition of acid until a total of 500-mL of HNO_3 has been added.
5. Evaporate to about 20 mL. Transfer to a 400-mL beaker with water.
6. Adjust the pH to 4 with 1:1 NH_4OH and proceed with Determination.

C. Feces ash.

1. Weigh 1 g of fecal ash into a 150-mL beaker. Add a weighed aliquot (about 0.1 g) of ^{133}Ba tracer solution and 1 mL of barium carrier solution.
2. Cover the ash with a small quantity of water and slowly add 10 mL of HNO_3 . Evaporate to a small volume on a medium hot plate.
3. Add about 25 mL of water. Add NH_4OH until a permanent hydroxide flock forms (3-5 mL).
4. Dissolve the flock in a few drops of HNO_3 .
5. Add 2 mL of NH_4Ac solution and 1 mL of acetic acid solution. Dilute to about 100-mL and proceed with **Determination**.

DETERMINATION

1. Add 1 mL of $(\text{NH}_4)_2\text{SO}_4$ solution and allow the sample to digest for 1 h at room temperature.
2. Filter by gravity on a 9 cm Whatman No. 42 filter paper. Wash the paper thoroughly with water. Discard the filtrate and washings.
3. Transfer the paper to a platinum dish. Dry the paper and then ash at 500°C for about 1 h.
4. Add 1 mL of H_2SO_4 and 2 mL of HF. Evaporate to SO_3 fumes.

5. Cool and transfer to a 90 mL centrifuge tube with water.
6. Police the dish and add the washings to the centrifuge tube.
7. Stir and let stand for 0.5 h.
8. Centrifuge at 2000 rpm for 1 h. Add one drop of 0.1% Aerosol OT. Decant carefully and discard the supernate.
9. Heat a solution of EDTA (300 g L⁻¹ EDTA) in an 85°C water bath.
10. Break up the BaSO₄ precipitate with a stirring rod.
11. Add 1 mL of 1:1 triethanolamine and 5 mL of the hot EDTA solution, and stir. Wash down the sides of the tube with water.
12. Digest in the steam bath for 15 min, stirring occasionally.
13. Transfer the solution to a 30-mL polyethylene bottle.
14. Dilute the sample to the same liquid level as a known aliquot (about 0.1 g) of ¹³³Ba solution diluted to 25 mL in a 30 mL polyethylene bottle.
15. Gamma count samples and standard on a flat crystal to determine the chemical yield of barium.
16. Transfer the sample solution to a radon bubbler.
17. De-emanate radon by bubbling with forming gas for about 10 min at 100 mL⁻¹ min as described in Procedure Ra-03-RC. Record the time as the starting time for the radon build-up period. Continue the analysis by the emanation technique.

LOWER LIMIT OF DETECTION (LLD)*

		A	B	C
Counter Efficiency	(%)	57.5	57.5	57.5
Counter Background	(cps)	0.0028	0.0028	0.0028
Yield	(%)	90	80	85
Blank	(cps)	0.0012	0.0020	0.0012
LLD (400 min)	(mBq)	0.33	0.45	0.39
LLD (1000 min)	(mBq)	0.17	0.29	0.15

*Reagent blanks must be analyzed with each set of samples.

Pulse ionization chamber:

A = Tap water

B = Urine

C = Feces

Ra-05-RC

RADIUM-224 IN URINE
(see Volume II)

Ra-06-RC

RADIUM-226 IN URINE AND WATER

Contact Person(s) : Isabel M. Fisenne

APPLICATION

This procedure is applicable to samples of urine and water. Small amounts of thorium are carried by the BaSO_4 and the method fails in the presence of ^{230}Th . Natural thorium does not interfere. Other α -emitting isotopes of radium also interfere.

Radium is initially separated from untreated water or urine by coprecipitation with calcium phosphate. Calcium and most other elements are removed by coprecipitation of radium on barium sulfate. Organic material is removed by ignition, silica is removed by volatilization with HF , and the radium-barium sulfate is reprecipitated.

Radium-226 in the barium sulfate precipitate is stored to allow the buildup of ^{222}Rn , ^{218}Po , and ^{214}Po . The equilibrated α activities are then measured with a scintillation counter. The instrument response is converted to Bq by application of corrections for counter background and efficiency and for self-absorption. Chemical recovery is measured gravimetrically and the ^{226}Ra activity is equivalent to one-fourth of the total Bq measured.

SPECIAL APPARATUS

1. Rings and discs - see Specification 7.2.
2. Teflon filter holders and filter funnels and sample mounts - see Specification 7.12.
3. Mylar film - see Specification 7.10.

SPECIAL REAGENTS

1. Barium carrier solution: 5 mg Ba mL⁻¹ - 9.51 g Ba(NO₃)₂ L⁻¹ of 1:99 HCl.

SAMPLE PREPARATION

A. Water.

1. Transfer 4 L of the sample to a 5 L stainless steel pot.
2. Add 1 mL of barium carrier solution and 4 mL of HNO₃.
3. Evaporate to near dryness, add additional aliquots of water and HNO₃, and continue until 50 L of sample have been treated.
4. Evaporate to about 100 mL, add 3-4 g of NH₄Ac, and adjust the pH to 5 with 1:1 NH₄OH.

B. Urine.

1. Transfer a measured volume of urine to a 250-mL centrifuge bottle and add 1 mL of barium carrier solution.
2. Add 2 mL of H₃PO₄. Adjust the pH to 9 with 1:1 NH₄OH. Stir, centrifuge, and discard the supernate.
3. Dissolve the precipitate with 10 mL of HNO₃. Dilute to about 100 mL with water.
4. Add 1 mL of H₃PO₄. Adjust the pH to 9 with 1:1 NH₄OH. Stir, centrifuge, and discard the supernate.
5. Dissolve the precipitate in a few mL of acetic acid and dilute to 100 mL with water. Adjust the pH to 5 with 1:1 NH₄OH.

DETERMINATION

1. Add 3-4 g of $(\text{NH}_4)_2\text{SO}_4$ with stirring. Digest for 12 h. Cool and filter by gravity on a 9 cm Whatman No. 42 filter paper. Wash with 0.5% H_2SO_4 . Discard the filtrate and washings.
2. Transfer the precipitate and filter to a platinum dish. Dry and ignite at 900°C .
3. Cool and add 2 mL of 1:1 H_2SO_4 and 5 mL of HF. Evaporate on a sand bath until SO_3 fumes appear.
4. Transfer the solution to a 40 mL, heavy walled centrifuge tube with 30 mL of H_2O and digest for 12 h. Centrifuge and discard the supernate.
5. Wash the precipitate with 10 mL of water. Centrifuge and discard the washings.
6. Slurry the precipitate with water and filter on a tared Whatman No. 42 filter paper.
7. Dry in an oven at about 150°C for at least 2 h.
8. Cool, weigh, and mount on a ring and disc with an α phosphor and Mylar.
9. Store for 30 days and count on an α -scintillation counter.

DATA PROCESSING AND ANALYSES

The ^{226}Ra disintegration rate is obtained from the counting rate of the equilibrated radium fraction through the following calculation:

$$\text{Bq} = R_s \text{ YTCE}$$

where R_s is the net counting rate of the sample, Y is the recovery factor, T is the self-absorption correction, E is the counter efficiency factor, and C is a theoretical conversion from total α activity to ^{226}Ra α activity.

Chemical recovery, Y, is obtained by weighing the final Ba sulfate precipitate. The calculation of the recovery factor is:

$$Y = \frac{x}{(w - t) f}$$

where x is the weight of barium added as carrier, w is the total weight of the final precipitate and filter paper, t is the weight of the filter paper, and f is the gravimetric factor which equals 0.588 mg barium per mg of barium sulfate.

Self-absorption correction, T, is used to normalize the self-absorption of the ^{226}Ra , ^{222}Rn , ^{218}Po , and ^{214}Po α activities in samples and standards to a common thickness (mg cm^{-2}). T is obtained by counting representative α emitters over the energy range of 4.8-8.8 MeV in precipitates of varying sample thicknesses. The correction is taken as the ratio of counting rates at an arbitrary minimum thickness to other thicknesses over the range of probable sample recoveries. Figure 1 is a typical composite plot of the correction obtained for ^{230}Th , ^{212}Pb , and ^{226}Ra activities for varying thicknesses of their oxalate, chromate, and sulfate derivatives, respectively.

Theoretical activity conversion factor, C, equals 0.25 after 30 days of buildup, when the three α -emitting progeny are in secular equilibrium with ^{226}Ra . However, the ratio of ^{226}Ra to total α activity at any time after the separation of radium may be calculated from the Bateman equation for buildup of ^{222}Rn .

Efficiency factor, E, is determined by α counting a known quantity of ^{226}Ra under sample conditions. The correction is taken as the ratio of the theoretical activity to the observed counting rate. The calculation is expressed as:

$$E = \frac{A}{R_s' T' C'}$$

where A is the theoretical activity of the standard, and R_s' is the net counting rate of the standard, T' is the self-absorption correction for the standard, and C' is the theoretical ratio of ^{226}Ra to total α activity in the standard.

An accompanying computational data sheet illustrates a procedure for routine calculation of ^{226}Ra activity rates. Experimental data are tabulated as they are derived and the calculations are performed on a step-by-step basis.

LOWER LIMIT OF DETECTION (LLD)*

Counter efficiency	(%)	50
Counter background	(cps)	1.67×10^{-5}
Yield	(%)	85
Blank	(cps)	1.67×10^3
LLD (400 min)	(mBq)	3
LLD (1000 min)	(mBq)	2

*Reagent blank must be analyzed with each set of samples.

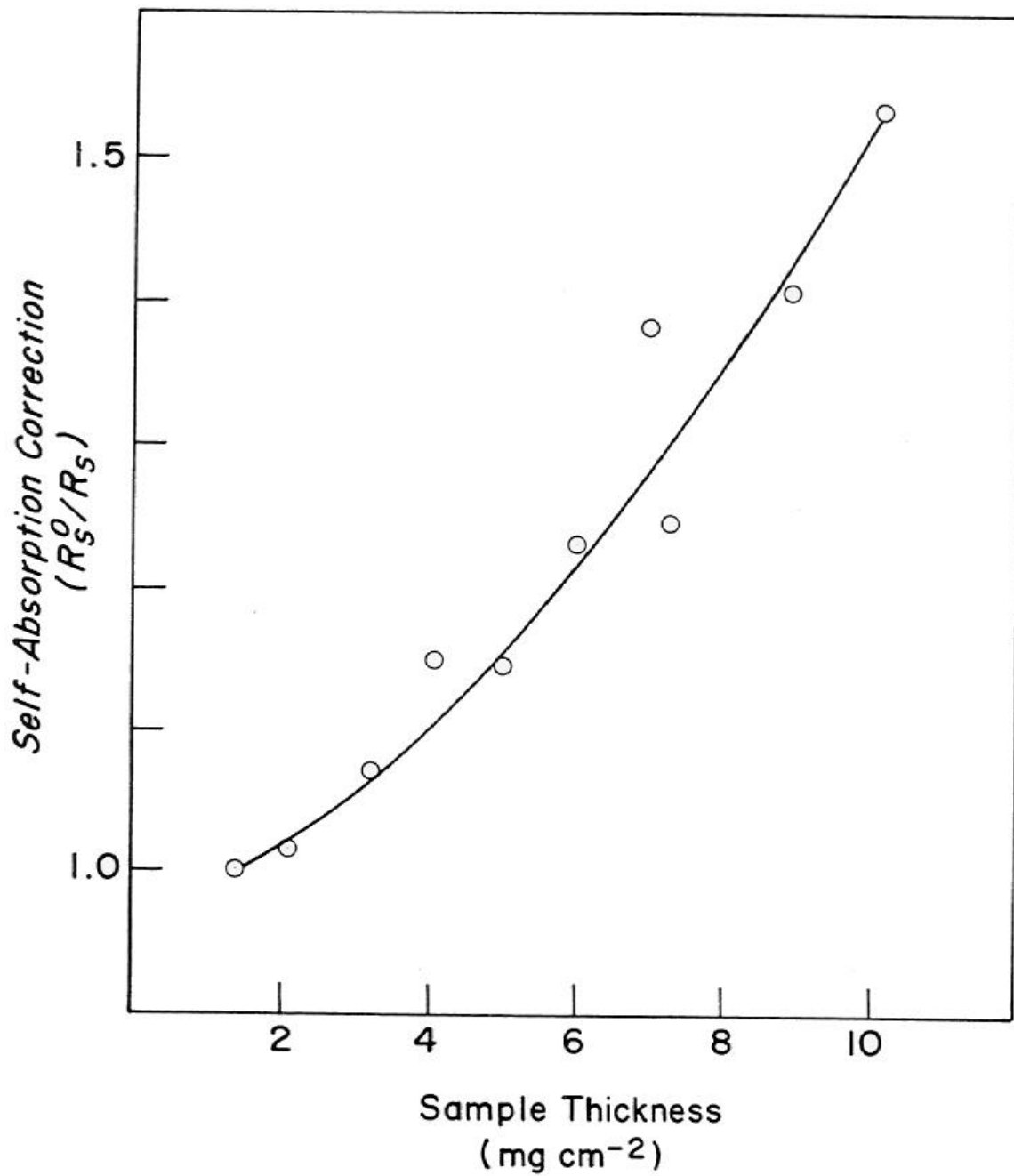


Figure 1. Self-absorption for α activities (4.8-8.9 MeV).

Date _____

Sample Number

		Operation						
1	Counter number	-						
	STANDARD							
2	Gross background count	-						
3	Count interval (s)	-						
4	Background (cps)	2/3						
5	Gross standard count	-						
6	Count time	-						
7	Standard (cps)	5/6						
8	Standard (net cps)	7-4						
	CORRECTIONS							
9	Gross weight (mg)	-						
10	Tare weight	-						
11	Net weight	9-10						
12	Weight of barium	11x0.59						
13	Carrier added	-						
14	Chemical yield factor (Y)	13/12						

Sample Number

[illegible]

Environmental Measurements Laboratory
U.S. Department of Energy

Date _____

Sample Number

		Operation						
1	Counter number	-						
3	Count interval (s)	Copy						
4	Background (cps)	Copy						
18	Efficiency factor (E)	Copy						
	SAMPLE COUNTING							
19	Gross sample count	-						
20	Count time	-						
21	Sample (cps)	19/20						
22	Sample (net cps)	21-4						
23	Sample (Bq)	22x18						
	CORRECTIONS							
24	Gross weight (mg)	-						
25	Tare weight	-						
26	Net weight	24-25						
27	Weight of barium	26x0.59						
28	Carrier added	-						
29	Chemical yield factor (Y)	28/27						
26	Net weight	Copy						
30	Thickness correction (T)	Graph						

Date _____

Sample Number

		Operation						
31	Corrected sample (Bq)	23x29x30						
	STANDARD							
32	Background/count interval	4/3						
33	Sample/count intervals (cps)	21/20						
34	S ²	32+33						
35	S for sample (net cps)	√34						
36	Total correction factor	18x29x30						
37	S for sample (Bq)	35x36						

Radon

Rn-01-RC

RADON-222 IN AIR AND BREATH SAMPLES

Contact Person(s) : Isabel M. Fisenne

APPLICATION

Procedures are presented which describe EML's method of sampling, counting, and calculating ^{222}Rn concentration in air and breath samples. When radium is present in the body, the gaseous progeny, ^{222}Rn ($t_{1/2} = 3.825$ d), will collect in the lungs and will be eliminated with exhaled breath.

One liter glass sampling flasks are provided to field personnel by EML for collecting breath or atmospheric ^{222}Rn samples. The ^{222}Rn sample is transferred to a pulse type ionization chamber, and after it is allowed to come into equilibrium with its progeny products, the sample is α counted. Two of the progeny, ^{218}Po and ^{214}Po , are α emitters and contribute to the total count.

SPECIAL APPARATUS

A. Sampling.

1. 1-L glass flasks with two large bore stopcocks per flask.
2. Tank of compressed, aged air with two-stage regulator.
3. Face mask - No. CS-6772 inhalator, modified to block the emergency intake and with the outlet modified to accept 9.5 mm ID rubber tubing (Mine Safety Appliance Co., Pittsburgh, PA).

4. Demand regulator - No. CS-46516 single stage or equivalent (Mine Safety Appliance Co., Pittsburgh, PA).

B. Analysis.

1. Platinum black catalyst (Baker and Co., Deoxo Units).
2. Drying tube with Drierite.
3. Flame arresters.
4. Capillary orifice.
5. Vacuum pump.
6. Tank of H₂ with two-stage regulator.
7. Tank of forming gas (85% N₂, 15% H₂) with two-stage regulator.
8. Sample introduction system including valves and piping.
9. Pulse type ionization chamber and associated electronic equipment.

SAMPLE COLLECTION

A. Radon in breath*

1. Set up the equipment as described in the above reference using 9.5 mm (3/8 in) rubber tubing on the inhalator outlet. Do not attach to sampling flask.
2. Clean facepiece with cotton and alcohol.
3. Set air pressure on two-stage regulator to 4.5 kg (10 lb).

* Taken from Harley *et al.*, 1951.

4. Have the subject hold the facepiece in place while you check for leaks, particularly around the bridge of the nose.
5. Have the subject breathe with the respirator for 5 min to flush the environmental air from his or her lungs. (This should be regular breathing. Do not ask for deep breaths.)
6. While the subject continues regular breathing, attach the sampling flask (with both stopcocks open) for a 1-min period, remove, and close stopcocks.
7. Repeat Step 6 for a duplicate sample.

B. Radon in the atmosphere.

1. Open both flask stopcocks.
2. Connect about 0.6 m of 9.5 mm (3/8 in) rubber tubing to one stopcock.
3. Inhale through the tubing and flask 20 times. Do not exhale through the flask. If convenient, a suction pump may be used.
4. Close both stopcocks.

MEASUREMENT EQUIPMENT PREPARATION

A. Sample oxidation.

Before transfer to the counting system, enough H_2 is added to the sample flask to completely remove O_2 (as H_2O) in the platinum catalyst. Because O_2 acts to quench the ionization produced by each α disintegration, even small amounts of it in the chamber will seriously affect the counting rate of a sample. Environmental air contains about 20% O_2 and the addition of 40 kPa (6 psi) of H_2 is theoretically sufficient for all samples. It has been our practice to add an excess of H_2 and therefore 70 kPa (10 psi) is usually added to each sample.

B. Flame arresters.

The removal of O_2 from the sample takes place in the platinum black catalyst where O_2 and H_2 combine to form H_2O . This combustion reaction generates a considerable amount of heat, and if allowed to strike back, the sample flask may explode. To prevent such explosions, flame arresters are placed between the catalyst and the sample. The flame arresters consist of a fine mesh copper wire screen and act to dissipate the heat of the reaction.

C. Capillary orifice.

A capillary orifice is placed in the line after the catalyst. This slows the passage of gas through the catalyst and insures complete combustion.

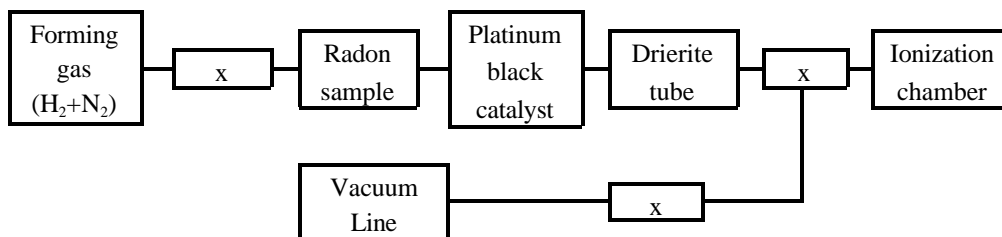
D. Drierite tube.

Water formed in the O_2 removal is collected in a Drierite tube. The Drierite is kept free of H_2O by evacuating the external piping of the system continuously when not transferring the samples.

E. Counting apparatus.

The ^{222}Rn counting apparatus consists of a sample introduction system, ionization chamber, preamplifier, amplifier, and count registering device. The ionization chamber counts almost 100% of the α disintegrations of ^{222}Rn and about 50% of the disintegrations of its progeny. Each chamber plus its sample introduction system has a capacity of 2 L and the chamber is operated at a potential of 1000 V. A mixture of H_2 (15%) and N_2 (85%) is used as a counting gas. The chambers are constructed of a specially selected, electropolished stainless steel and have a background count of about 10 counts h^{-1} and an efficiency of about 6215 counts h^{-1} for 1 Bq of ^{222}Rn .

A block diagram of the counting system and external apparatus is shown below.



x indicates valve or stopcock.

The pulses from the ionization chamber are fed to an EML-built preamplifier, amplifier, and control unit. Two Tattletale Clever counters are interfaced to a PC.

DETERMINATION

1. Connect sample flask to H₂ tank with 9.5 mm (3/8 in) rubber tubing.
2. Raise gauge pressure to 70 kPa (10 psi) gauge.
3. Open flask stopcock to tank to admit H₂ to the flask.
4. Close stopcock and tank valve.
5. Raise the forming gas line pressure to 70 kPa (10 psi) gauge and bleed the line and rubber tubing leading to sample inlet.
6. Connect one flask stopcock to the forming gas line with the above rubber tubing, the other to the counting system with another section of 9.5 mm (3/8 in) rubber tubing.
7. Open the ionization chamber and the vacuum line valve to evacuate the counting chamber, external piping, and the rubber tubing between the counting system and the flask.
8. Close the vacuum line valve when system reaches minus 10.1 kPa of Hg gauge pressure.

9. Open the flask stopcock to allow the sample to enter the counting system. Allow pressure equilibration (indicated by pressure gauge).
10. Check platinum catalyst by touch to assure that combination of H_2 and O_2 has occurred.
11. Close the flask stopcock to the counting system.
12. Open the stopcock to the forming gas line. Allow forming gas to come to pressure in the flask.
13. Repeat Steps 5 and 7 until the gauge indicates atmospheric pressure.
14. Open the stopcock to the forming gas line, then attach the stopcock to the counting system. Allow forming gas to flow until the gauge pressure reaches 35 kPa (5 psi).
15. Close all valves and remove flask and tubing from system.
16. Turn on ionization chamber high voltage.
17. Count the sample for at least 14 h.

DATA PROCESSING AND ANALYSES

1. Discard the first 5 h of counting data (equilibration period for ^{222}Rn and progeny).
2. Determine the gross count over the remaining counting period.
3. Calculate net counts per hour per sample by determining gross sample counts per hour and subtracting background counts per hour.
4. Divide net counts per hour by the chamber standardization value of net counts per hour per Bq of ^{222}Rn .

5. Using the midpoint of the counting interval as the time of counting, extrapolate the value obtained to the time of sampling. Figure 1 may be used for this calculation.

STANDARDIZATION

Each unit is standardized several times a year with ^{222}Rn from a radium solution obtained from the National Institute of Standard and Technology (NIST). This solution is diluted and split into aliquots which are placed in ^{222}Rn bubblers (see Specification 7.8). The ^{222}Rn is allowed to build up for a known period before the standard is used.

The ^{222}Rn standard is transferred to the chamber by emanation. The bubbler is first attached to the external feed system. When the ionization chamber and external system are evacuated, the vacuum line is shut off from the system and the bubbler outlet stopcock opened. The inlet stopcock is then opened and forming gas flushes the ^{222}Rn into the chamber until the system is brought to atmospheric pressure.

At equilibrium, there are three α disintegrations per ^{222}Rn disintegration, however, two of these are from the particulate α -emitting progeny. Since these α disintegrations deposit on the walls of the ionization chamber, they are counted with a maximum efficiency of 50%. One becquerel of ^{222}Rn in the ionization chamber thus has a theoretical counting rate of 7190 counts h^{-1} . Actually, the ionization chambers in this Laboratory yield a counting rate of 6215 counts h^{-1} Bq^{-1} of ^{222}Rn in equilibrium with its progeny or an overall efficiency of 86%.

LOWER LIMIT OF DETECTION (LLD)

Counter Efficiency	(%)	57.5
Counter Background	(cps)	0.0028
Yield	(%)	-
Blank	(cps)	-
LLD (400 min)	(Bq)	0.01
LLD (1000 min)	(Bq)	0.07

REFERENCE

Harley, J. H., E. Jetter and M. Eisenbud
"A Method of Obtaining Reproducible Breath Radon Samples"
Arch. Ind. Hyg. Occ. Med., 4, 1-9 (1951)

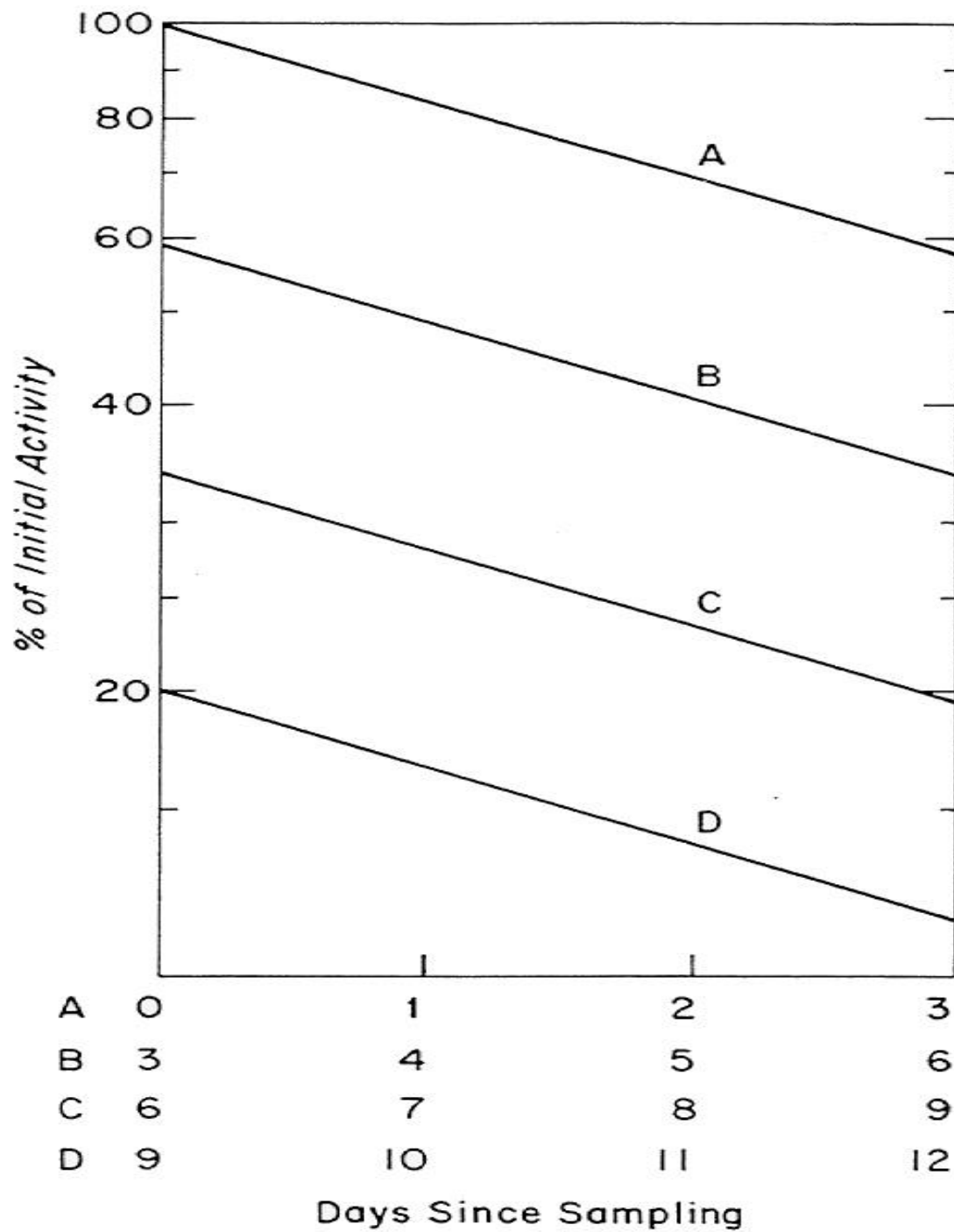


Figure 1. Decay correction for radon from the midpoint of the counting interval to collection time.

Strontium

Sr-01-RC

STRONTIUM-89
(see Volume II)

Sr-02-RC

STRONTIUM-90
(see Volume II)

Sr-03-RC

STRONTIUM-90 IN ENVIRONMENTAL MATRICES

Contact Person : Marie Lawrence

APPLICATION

This procedure is applicable to the preparation, separation, and analysis of vegetation, water, air filters and soil.

Strontium is separated from calcium, other fission products and natural radioactive elements. Fuming HNO_3 separations remove the calcium and most of the other interfering ions. Radium, lead and barium are removed with barium chromate. Traces of other fission products are scavenged with iron hydroxide. After the $^{90}\text{Sr} + ^{90}\text{Y}$ equilibrium has been attained, the ^{90}Y is precipitated as the hydroxide and converted to the oxalate for counting on a low-background gas proportional beta counter. Chemical yield is determined with ^{85}Sr tracer by counting in a gamma well detector.

SPECIAL APPARATUS

1. Teflon filter holder or filter funnel and sample mount - see Specification 7.12.
2. Rings and discs - see Specification 7.2.
3. Magnetic stirrers with Teflon-coated magnet bars.
4. Mylar film - see Specification 7.3.
5. Glass fiber filters - see Specification 7.8.
6. Fisher filtrator, Fisher Chemical Company, Pittsburgh, PA 15219-4785.

7. Polyethylene reference bottles, 30-mL narrow mouth to fit in a gamma well detector.

SPECIAL REAGENTS

1. Strontium carrier, 20 mg Sr mL⁻¹ - dissolve 48.4 g Sr(NO₃)₂ in 1 L of 1:99 HNO₃.
2. Yttrium carrier, 10 mg Y mL⁻¹ - dissolve 12.7 g of highest purity Y₂O₃ in a minimal amount of HNO₃; use heat if necessary. Filter, if necessary, and add water to make 1 L of solution. See the APPENDIX for the yttrium carrier counting check.
3. Iron carrier, 5 mg Fe mL⁻¹ - dissolve 5 g Fe wire in 1:1 HCl and dilute to 1 L with 1:99 HCl, or dissolve 34.7 g Fe(NO₃)₃·9H₂O in 1 L of 1:99 HNO₃.
4. Barium carrier, 10 mg Ba mL⁻¹ - dissolve 9.5 g Ba(NO₃)₂ in water and dilute to 0.5 L.
5. Barium buffer solution - 500 mL 6M acetic acid (glacial HOAC) plus 1 L of 6M NH₄OAc plus 0.5 L Ba carrier (10 mg mL⁻¹).
6. Calcium carrier, 200 mg Ca mL⁻¹ - dissolve 500 g calcium carbonate (CaCO₃) in a minimum of HCl and dilute to 1 L with water.
7. ⁸⁵Sr tracer, about 7x10⁵ Bq L⁻¹, in a well counter, this tracer should provide about 150 counts sec⁻¹ mL⁻¹.
8. Sodium carbonate solution, 1M - dissolve 106 g Na₂CO₃ in H₂O and dilute to 1L.
9. Sodium carbonate solution, 2M - dissolve 212 g Na₂CO₃ in H₂O and dilute to 1L.
10. Sodium chromate solution, 0.3M - dissolve 50 g Na₂CrO₄ in H₂O and dilute to 1L.
11. 50% sodium hydroxide solution - slowly dissolve 500 g NaOH in 500 mL of H₂O in a plastic liter bottle immersed in a beaker of ice water.

SAMPLE PREPARATION

A. Water

1. Transfer an aliquot of sample water to an appropriate sized beaker (use deionized water for the blank).
2. Add 1 mL (20 mg) strontium carrier to the blank and the sample.
3. Add exactly 1.00 mL of ^{85}Sr tracer to three 30-mL plastic bottles, the blank and the sample.
4. Fill the plastic bottles with equal volumes of 1M HCl. Set bottles aside. They will serve as references when determining the strontium yield.
5. Evaporate the samples to dryness. Add 10-mL volumes of concentrated nitric acid to the dried residue, and evaporate repeatedly to remove any trace of HCl due to the reagents added.
6. Dissolve the final residue in 8M HNO_3 . If the sample is not in a 400-mL beaker, quantitatively transfer the sample with water to a 400-mL beaker containing a Teflon-coated magnetic stirring bar. Dilute the sample to 200 mL with additional water.
7. Place the beaker on a magnetic stirrer/hot plate and stir. Adjust the pH to 5-6 with 50% NaOH. While continuing to stir, add 15 mL of 2M Na_2CO_3 . Heat the sample to just below boiling and stir for 30 min.
8. Remove the sample from the hot plate and allow the precipitate to settle overnight.
9. Place a small glass fiber filter backed with a Whatman No. 42 filter paper of the same size into a Büchner funnel. Mount the funnel on a 500 mL filter flask.
10. Filter the sample by vacuum through the funnel. Wash the carbonates retained on the filter with 1M Na_2CO_3 solution. Discard the filtrate.

11. Release the vacuum and transfer the funnel to a clean filter flask. Apply the vacuum. Dissolve the carbonates on the filter with hot 8M HNO_3 . Wash the filter with water.
12. Transfer the filtrate to a 400 mL beaker, rinsing with 8M HNO_3 . Evaporate the solution to dryness.
13. Proceed to **Determination, Fuming HNO_3 Separation**

B. Air Filters

1. Place the air filter in a 400-mL beaker (use a dry beaker for the blank).
2. Add exactly 1.00 mL of ^{85}Sr to three 30-mL plastic reference bottles, the blank and the sample.
3. Fill the plastic bottles with equal volumes of 1M HCl . Set bottles aside. (The same three reference bottles may be used for water and air filters if the analyses are done simultaneously.)
4. Add 20 mg (1 mL) strontium carrier to the blank and the sample.
5. Add 150 mL HNO_3 and 50 mL HCl . Reflux on a hot plate until clear and colorless. Evaporate to a volume of ~ 100 mL.
6. Add 100 mL of deionized water. Cool the sample to room temperature. Filter by gravity through a Whatman No. 42 filter. Wash the filter with 8M HNO_3 .
7. Evaporate the filtrate to dryness. Add 20 mL volumes of concentrated nitric acid to the dried residue, and evaporate repeatedly to remove HCl . Continue with Step 6, Section A, **Water**.

C. Soil (NaOH-HCl method) - see Note 1

1. Weigh out enough soil to generate an activity at least 10 times background (ideally 100 times) into an appropriate sized beaker containing a Teflon-coated magnetic stirring bar (see chart below). Add water to about a quarter of the beaker's volume and add 5-10 mL (100-200 mg) strontium carrier solution. Place the beaker on a magnetic stirrer.
2. To each of three 30-mL plastic reference bottles and to the sample add 1.00 mL of ^{85}Sr tracer solution. Fill the reference bottles to the same level with 1M HCl.
3. Stir the sample. While continuing to stir, add a sufficient amount of 50% NaOH to make the solution 1N NaOH. (see chart below)
4. Cover with a watch glass and stir for 10 min. Reflux overnight on a warm hot plate.
5. Remove the beaker from the hot plate and allow to cool. While stirring, cautiously add HCl, 1 mL at a time until the reaction slows, to make the solution 6M acidic (see chart below). If analyzing highly calcareous soils, an additional quantity of HCl should be added to replace the acid required to decompose the carbonates. If necessary, add a few drops of n-octyl alcohol to reduce foaming.

Activity (Bq kg ⁻¹)	Sample size (g)	Beaker size (mL)	Water (mL)	Carrier (mL)	50% NaOH (mL)	HCl (mL)
~500	5-10	250	70	5	4	90
~100	15-20	400	100	5	6	130
~50	30-40	800	200	5	11	260
~10	100	1000	250	5	14	320

6. Digest the sample overnight on a warm hot plate. Remove the beaker from the hot plate and cool.

7. Filter the sample under vacuum using a Whatman No. 42 filter paper backed by a glass fiber filter. Wash with approximately 100 mL hot 6M HCl, followed by 60 mL hot H₂O.
8. Turn off the vacuum. Return the soil residue and the filter paper to the original beaker.
9. Quantitatively transfer the filtrate and washes to an appropriate sized beaker, rinsing with water, and place on a warm hot plate to reduce the volume.
10. Remove the filtrate from the hot plate. Add 20-50 mL of HNO₃. Cover with a watch glass and place back on the hot plate. Turn the heat up to high. Continue adding HNO₃ until the conversion is complete, as indicated by the absence of brown fumes after the addition of HNO₃.
11. Add water to about a quarter of the beaker's volume to the beaker containing the filter paper and soil residue. Repeat Steps 3-7.
12. Transfer the second filtrate to the beaker containing the original filtrate. Convert to HNO₃ as in Step 10.
13. Reduce the volume of the combined filtrates to ~50 mL or until salting out begins to occur. Add ~100 mL (or twice the volume) of water, stir and cool to room temperature. If cloudy, filter under vacuum through two glass fiber filters, washing with hot 1-2M HNO₃. Discard the filters.
14. Quantitatively transfer the filtrate to a large (800-1500 mL) beaker containing a magnetic stirring bar, rinsing with water. Place the beaker on a magnetic stirrer/hot plate and stir while warming the solution.
15. Add approximately 5 g of H₂C₂O₄ (oxalic acid) L⁻¹ and continue to stir until the salt completely dissolves.
16. While stirring, adjust the pH to 5.5-6.0 with NH₄OH. If the mixture turns brown due to the presence of FeO(OH), add just enough H₂C₂O₄ to bring back the green color and readjust the pH. Repeat this process, using decreasing quantities of H₂C₂O₄, until

the last pH adjustment does not result in the brown color. (**Note:** At this point, there should be enough $\text{H}_2\text{C}_2\text{O}_4$ to precipitate the insoluble white oxalates and to complex the Fe^{+3} ion, but not enough to cause crystallization of the $(\text{NH}_4)_2\text{C}_2\text{O}_4$ upon cooling.) Finish by adding several grams of oxalic acid as excess and adjust the pH again. Stir for 30 min on a warm hot plate.

17. Turn off the stirrer, remove the beaker from the hot plate, and allow the precipitate to settle overnight.
18. Add 5 mL of Ca carrier solution (1g Ca), stir the supernatant very gently and allow the fresh precipitate to settle for 15-20 min.
19. Filter the sample by gravity through a large Whatman No. 42 filter paper. Wash the beaker with H_2O , adding the washes to the funnel. Wash the precipitate with water until the filtrate is colorless.
20. Transfer the filter paper and precipitate to a 600-mL beaker. Add 100 mL of HNO_3 . Cover with a watch glass and wet ash the oxalates until clear and colorless or oxidation seems complete, adding more HNO_3 as necessary.
21. Add an equal volume of water and stir on a magnetic stirrer. If cloudy, filter through two glass fiber filters washing with 8M HNO_3 , followed by water. Evaporate to dryness.
22. Proceed to **Determination, Fuming HNO_3 Separations.**

Note: This method was developed at the U.S. Department of Agriculture Soil Survey Laboratory, Soil Conservation Service, Beltsville, MD. Comparative soil analyses at EML showed that the ^{85}Sr tracer could be completely equilibrated with ^{90}Sr present in the soils when consecutively treated with NaOH and HCl. The NaOH-HCl method yielded results equal to those obtained with the complete dissolution method.

D. Vegetation (dry ashing).

1. Weigh an aliquot of up to 10 g of vegetation into a tared 250-mL porcelain crucible.
(**Note:** After ashing, several aliquots can be combined to provide the desired sample

size.) Place each crucible in a muffle furnace with the crucible cover slightly ajar. Increase the temperature of the furnace at a rate of $0.80^{\circ}\text{C min}^{-1}$ to 250°C . Maintain this temperature for 30 minutes. Increase the temperature at a rate of $10^{\circ}\text{C min}^{-1}$ to 600°C . Maintain this temperature for 960 min to completely ash the sample. Cool the crucible and weigh it to determine the percent ash. Ash content for replicate crucibles should vary by not more than 4%.

2. Transfer the ashed vegetation to a beaker using 8M HNO_3 to dissolve the ash and rinse the crucible. Add 1 mL of Sr carrier (20 mg).
3. Add 1.00 mL of ^{85}Sr tracer to the blank, the sample and each of three 30-mL plastic reference bottles. Fill the bottles to the same level with 1M HCl .
4. Cover with a watch glass and reflux on a hot plate until there is no evidence of remaining organic matter, adding HNO_3 or H_2O_2 as necessary.
5. Evaporate to near dryness. Add 50 mL of 8M HNO_3 . Filter by gravity through a Whatman No. 42 filter paper into a beaker, washing with 8M HNO_3 . Continue with Step 6 below.

E. Vegetation (wet ashing).

1. Weigh an aliquot of vegetation into an appropriate sized beaker. (For 100-300 g, use a 3000-mL beaker.) Add 1 mL of Sr carrier (20 mg).
2. Add 1.00 mL of ^{85}Sr tracer to the blank, the sample and each of three 30-mL plastic reference bottles. Fill the bottles to the same level with 1M HCl .
3. Slowly add 500 mL of 8M HNO_3 . Control the foaming, if necessary, by adding a few drops of n-octyl alcohol. Cover with a watch glass and place on a low temperature hot plate overnight to maintain a slow reaction, stirring as necessary to break up the foam. Gradually increase the temperature of the hot plate, adding HNO_3 and continuing to reflux until the reaction is complete, as indicated by the absence of brown nitrogen oxide gas.

4. Remove from the hot plate. Slowly add enough HCl to equal one third the volume of HNO_3 still in the beaker. Allow the mixture to react at room temperature for 15 min, then cover with a watch glass and heat on a low temperature hot plate overnight with occasional stirring.
5. Remove the sample from the hot plate and add an equal volume of water. Allow the sample to cool to room temperature. Filter by gravity through a large Whatman No. 42 filter paper into a beaker. Wash with 8M HNO_3 .
6. Evaporate the filtrate to dryness. Dissolve the residue in a minimum of 8M HNO_3 . Quantitatively transfer the solution to a 400-mL beaker containing a Teflon-coated magnetic stirring bar, rinsing with H_2O . Dilute the solution to 200 mL with additional H_2O .
7. Place the beaker on a magnetic stirrer/hot plate and stir. Adjust the pH to 5-6 with 50% NaOH. While continuing to stir, add 15 mL of 2M Na_2CO_3 . Heat the sample to just below boiling and stir for 30 min.
8. Remove the sample from the hot plate and allow the precipitate to settle overnight.
9. Place a small glass fiber filter backed by a Whatman No. 42 filter paper of the same size into a Büchner funnel. Mount the funnel on a 500 mL filter flask.
10. Filter the sample by vacuum through the funnel. Wash the carbonates retained on the filter with 1M Na_2CO_3 solution. Discard the filtrate.
11. Release the vacuum and transfer the funnel to a clean filter flask. Apply the vacuum. Dissolve the carbonates on the filter with hot 8M HNO_3 . Wash the filter with water.
12. Transfer the filtrate to a 400 mL beaker, rinsing with 8M HNO_3 . Evaporate to dryness.
13. Proceed to **Determination, Fuming HNO_3 Separations.**

DETERMINATION

A. Fuming HNO_3 separations.

1. Dissolve the residual salt in H_2O and some fuming HNO_3 , while stirring on a magnetic stirrer. When dissolved, add additional fuming HNO_3 to precipitate $\text{Sr}(\text{NO}_3)_2$. The first two separations require concentrations of $> 75\%$ HNO_3 , subsequent separations require less HNO_3 (see chart below). Water and air filters usually require two separations. Large quantities of soils with a high Ca content may require up to five or more fuming HNO_3 separations.

Separation	Water (mL)	Fuming HNO_3 (mL)	% HNO_3	final volume (mL)
1st	40	25 + 195	80.1	260
2nd	60	25 + 195	76.0	280
3rd	40	25 + 115	75.4	180
4th	30	105	75.4	135
5th	23	77	74.9	100

2. Place a dry (very important to prevent sample loss) 5.5-cm glass fiber filter (for smaller volumes a 4.25-cm filter) in a dry Büchner funnel and mount the funnel in a 1-L filter flask.
3. Suction filter the sample into the flask. Turn off the vacuum. Transfer the funnel to a Fisher filtrator, placing an appropriate sized beaker underneath (for the last filtration, use a 40-mL heavy-wall conical centrifuge tube (C-tube)). Apply a vacuum while dissolving the precipitate on the filter with water into the beaker. Use additional water to complete the transfer of any residue in the original beaker to the funnel and subsequently into the beaker or C-tube. Proceed with Step 4 or 5.
4. Evaporate the sample solution to dryness if another fuming HNO_3 separation is desired, and repeat Steps 1 to 3 using smaller volumes as indicated in the chart.

5. If the sample solution is now in a C-tube, place the tube in a hot water bath and adjust the volume to ~20 mL. Proceed with **First Milking**.

B. First milking.

1. Add 1 mL of iron carrier solution to the separated strontium fraction in the centrifuge tube. Stir the solution and place the tube in a 90°C water bath to warm.
2. While stirring, adjust the pH of the sample to 8 with NH_4OH . Remove the stirring rod, rinsing with H_2O . Remove the centrifuge tube from the water bath and cool to room temperature in a cold water bath.
3. Centrifuge the sample at 2000 rpm for 5 min. Decant the supernate into a second 40-mL centrifuge tube. Reserve the supernate for Step 6 and note the hour and date of this initial OH^- precipitation as **first milk separation time**.
4. Dissolve the precipitate in the first centrifuge tube in a few drops of HCl and dilute to 10 mL with H_2O . Stir the solution and warm the tube in the hot water bath.
5. While stirring, adjust the pH of the sample to 8 with NH_4OH . Remove the stirring rod, rinsing with H_2O . Remove the centrifuge tube from the water bath and cool to room temperature in a cold water bath.
6. Centrifuge the sample at 2000 rpm for 5 min. Decant and combine the supernate with the supernate reserved from Step 3. Evaporate to reduce the volume to 20 mL. Discard the precipitate.
7. While stirring, add 4 mL of barium buffer solution to the sample. If necessary, adjust the pH of the sample to 5.5 with either 6M HCl or NH_4OH (see **Note 1**).
8. Return the centrifuge tube to the hot water bath. While stirring vigorously, add 1 mL of 0.3M Na_2CrO_4 dropwise to the sample (see **Note 2**). Allow the sample to digest in the hot water bath for 10 min or longer to allow a good precipitate to form.
9. Remove the stirring rod, rinsing with H_2O . Remove the sample tube from the hot water bath and cool in a cold water bath.

10. Centrifuge the tube at 2000 rpm for 5 min. Decant the supernate into a 30-mL polyethylene bottle. Discard the precipitate.
11. Add 10-15 drops of HCl and exactly 1.00 mL of yttrium carrier solution to the sample in the polyethylene bottle and enough water to bring the volume of the solution to the same level as in the reference bottles.
12. Proceed to **Strontium-85 yield determination**.

Notes:

1. The pH of the solution is critical at this point. Complete precipitation of BaCrO_4 will not occur in a more acidic solution and strontium will partially precipitate in more basic solutions.
2. If large quantities of barium are present in the sample, only a partial precipitation of the Ba as BaCrO_4 may occur. The sample is centrifuged and the supernate decanted into another 40-mL centrifuge tube. The precipitation is completed by the dropwise addition of 0.3M Na_2CrO_4 to the supernate and the analysis is continued with Step 10.

C. Strontium-85 yield measurement.

1. Measure the activity of the three reference aliquots, the blank and the sample with a NaI(Tl) crystal gamma detector, collecting at least 10^4 counts.
2. After subtracting the background counts, calculate the ^{85}Sr yield of the sample by dividing the sample counts by the average of the three reference counts.
3. Store the sample for 2 weeks to allow ^{90}Y to reach secular equilibrium with ^{90}Sr (see **Note**).

Note: The **first milk separation time** noted in Step 3, **First milking**, is the start of the yttrium ingrowth period. In order to correct for less than complete buildup of ^{90}Y , a correction factor is included in the calculations.

D. Second milking.

1. Quantitatively transfer the sample from the polyethylene bottle to a 40-mL, heavy-walled, conical centrifuge tube with a minimum of H_2O . Stir the solution and place the tube in a 90°C water bath to warm.
2. While stirring, adjust the pH of the sample to 8 with NH_4OH . Add six drops of H_2O_2 and heat for 1 h. Remove and rinse the stirring rod. Remove the centrifuge tube from the water bath and cool to room temperature in a cold water bath.
3. Centrifuge the sample for 5 min at 2000 rpm. Decant the supernate into another 40-mL centrifuge tube. Record the hour and date of the precipitation as **second milk separation time**.
4. Dissolve the precipitate in the centrifuge tube with a few drops of HCl and stir. Dilute the sample to 15 mL with H_2O . Stir the solution and warm the tube in the hot water bath.
5. While stirring, adjust the pH of the sample to 8 with NH_4OH . Remove and rinse the stirring rod. Remove the centrifuge tube from the water bath and cool to room temperature in a cold water bath.
6. Centrifuge the sample for 5 min. Decant and combine the supernate with the supernate reserved from Step 3. Return the combined supernates to the hot water bath and reduce the volume to 20 mL. Transfer to a 30-mL polyethylene bottle and set aside for possible future milking.
7. Add four drops of HCl to the precipitate and stir until it dissolves. Add 25 mL of H_2O , stir and heat in the hot water bath.
8. Add 1 mL of strontium carrier (20 mg Sr) to serve as a holdback carrier. While stirring, adjust the pH to 8 with NH_4OH .
9. Remove and rinse the stirring rod. Remove the sample tube from the hot water bath and cool in a cold water bath.

10. Centrifuge the tube at 2000 rpm for 5 min. Decant and discard the supernate.
11. Add three drops of HCl to dissolve the precipitate, and 25 mL of H₂O.
12. Stir the sample and place the tube in a hot water bath. Add 1 mL of saturated H₂C₂O₄ (oxalic acid) solution.
13. Adjust the pH to 2-3 by the dropwise addition of NH₄OH with vigorous stirring. Digest the sample in the hot water bath for 1 h.
14. Rinse and remove the stirring rod from the tube, and cool it to room temperature in cold water.
15. Centrifuge the tube at 2000 rpm for 10 min. Decant and discard most of the supernate.
16. Dry a 2.8-cm Whatman No. 42 filter paper on a 110°C hot plate or in an 110°C oven, cool and weigh to the nearest 0.1 mg.
17. Using a Teflon filter funnel assembly, filter the precipitate by suction through the weighed 2.8-cm Whatman No. 42 filter paper, backed by a 2.8-cm glass fiber filter, completing the transfer with a minimum amount of water. Wash the precipitate with 95% ethanol.
18. With the suction on, remove the filter funnel. Carefully separate the Whatman filter with the precipitate from the glass fiber filter backing. Place the filter paper with the precipitate on a 110°C hot plate. Turn off the vacuum and discard the glass fiber filter. Discard the filtrate.
19. Dry the filter with precipitate to a constant weight to determine the gravimetric yield.
20. Carefully mount the filtered precipitate on a nylon disc, cover with Mylar, and fasten the assembly with a nylon ring.
21. Measure the sample in a low-level gas flow proportional counter, recording the hour and date of the beginning of the measurement period.

22. Collect at least 10,000 counts, disregarding the first 200 min (2 cycles) of counting to eliminate possible interference from any ^{222}Rn progeny present due to the filtration process. Proceed to calculations.

E. Gravimetric yttrium yield measurement.

1. Standardize triplicate 10-mL aliquots of the original yttrium carrier solution each time a fresh batch is made by precipitating the oxalate as described above and filtering through a fine (grade F), tared, sintered, glass filter crucible that has been dried to a constant weight.
2. Determine the weight of the yttrium oxalate precipitated from the sample as described in Steps 15-19 of **Second Milking**. The yttrium yield is the ratio of the weight of the sample oxalate to the standardized weight of the oxalate precipitated from the carrier solution.

CALCULATIONS

The β counting data obtained from the ^{90}Y precipitate must be corrected to give the activity of the ^{90}Sr in the sample. The corrections include those for ingrowth of ^{90}Y , counter background, ^{90}Y efficiency, strontium yield, yttrium yield, and ^{90}Y decay. ^{90}Y beta emissions are very energetic and are always counted with approximately the same mass of precipitate, so no correction for self-absorption is necessary.

The strontium yield is ordinarily determined by measuring the recovery of ^{85}Sr tracer added to the sample. Since the ratio of sample counts to counts from an aliquot of the original ^{85}Sr tracer solution is used to determine yield, there is no need to know the radioactivity rate of the tracer or to apply decay corrections for ^{85}Sr .

The activity of a sample of ^{90}Sr over a time interval, t , is

$$\int_0^t A dt' = \int_0^t A_0 e^{-\lambda t'} dt'$$

where A_0 is the initial activity of the sample. Integrating and rearranging to solve for A_0 yields:

$$A_0 = \left(\int_0^t A dt' \right) \cdot \frac{\lambda}{1 - e^{-\lambda t}}$$

The half-life of ^{90}Sr is quite large (29 y), so A_0 is essentially constant throughout the period of chemical separation and analysis. After 2 weeks, a sample of ^{90}Sr will be in secular equilibrium with its daughter, ^{90}Y , and the activities of the two nuclides will be equal. The quantity under the integral sign in the last equation above is the (corrected) measured activity of the separated ^{90}Y over the time period from separation to end of counting:

$$\int_0^t A dt' = \frac{N_y - B \cdot dt_c}{R_y \cdot R_{Sr} \cdot I_y \cdot D_y \cdot E_c}$$

To obtain A_0 , this quantity is multiplied by the factor

$$\frac{\lambda_Y}{1 - e^{-\lambda_Y \cdot dt_c}}$$

where:

λ_Y = decay constant of ^{90}Y (0.0108 h^{-1})

dt_c = total count time minus two 100-minute cycles (see **Note**)

N_y = total counts from all cycles except the first two (see **Note**)

B = counter background for the matrix used (^{90}Y -oxalate)

R_y = yttrium yield fraction

R_{sr} = strontium yield fraction

I_y = ^{90}Y ingrowth fraction = $1 - e^{-0.0108 \cdot dt1 \rightarrow 2}$ = fraction of ^{90}Y produced during the time from extraction of ^{90}Sr ("1st milk") to separation of ^{90}Y from ^{90}Sr ("2nd milk").

D_y = ^{90}Y decay fraction = $e^{-0.0108 \cdot dt2 \rightarrow c_0}$

E_c = counter efficiency for ^{90}Y -oxalate (counts min^{-1} dpm^{-1})

$dt1 \rightarrow 2$ = 1st milk to 2nd milk time

$dt2 \rightarrow c_0$ = 2nd milk time to start of counting plus two 100-min cycles (see **Note**)

Note: The first two cycles are ignored to allow for the decay of short-lived beta-emitting daughters from any radon-222 that may have attached to the Y-oxalate mount during preparation.

The calculated activity of the blank is subtracted from the calculated activity of the sample. The result is converted to appropriate units and divided by the sample size to obtain the activity concentration of the sample.

To check the radiochemical purity of the ^{90}Y -oxalate precipitate, a weighted linear regression analysis is done on the counting data, with $\ln(\text{counts} - \text{background counts})$ plotted against time. The weighting factor is the variance of the dependent variable:

$$\text{Weighting factor} = \text{Var}(\ln(c - c_{bkg})) = \frac{c + (\sigma_{c_{bkg}})^2}{(c - c_{bkg})^2}$$

where:

- C = sample counts
 C_{bkg} = background counts
 σ_{Cbkg} = standard deviation of background counts

The slope of the weighted regression line is equal to λ_Y , the decay constant of ^{90}Y .
 The value for λ_Y obtained from the regression analysis is compared to the known value of 0.0108 h^{-1} .

All calculations are done by computer.

LOWER LIMIT OF DETECTION (LLD)

Counter Efficiency	(%)	40
Counter Background	(cps)	0.005
Yield (Sr)	(%)	80
Yield (Y)	(%)	95
Blank	(cps)	
LLD (400 min)	(Bq)	0.007
LLD (1000 min)	(Bq)	0.004

APPENDIX

YTTRIUM CARRIER COUNTING CHECK

To verify that the carrier solution contains only stable yttrium, complete the following procedure:

1. Pipette 1 mL of yttrium carrier into each of three 40-mL centrifuge tubes. Dilute to 20 mL with H₂O.
2. Heat in a water bath to about 90°C. While stirring, adjust the pH to 8 with NH₄OH. Digest for 10 min and cool in a cold water bath.
3. Centrifuge for 5 min. Decant and discard the supernate. Proceed with Steps 11-22 of **Second Milking**.

Sr-04-RC

STRONTIUM-90 IN WATER CONTAINING OTHER RADIOISOTOPES BY Cerenkov COUNTING

Contact Person(s) : Salvatore C. Scarpitta

APPLICATION

The following procedure is used in the EML Quality Assessment Program (QAP; Sanderson and Greenlaw, 1996) for water or gross alpha/beta samples containing ^{90}Sr . This procedure was developed by Jimmy Chang, Institute of Nuclear Energy Research, Taiwan, and was tested at EML using NIST $^{90}\text{Sr}/\text{Y}$ reference materials and ^{90}Sr contained in QAP water samples. It allows for the rapid determination of ^{90}Sr ($\beta_{\text{max}} = 0.546 \text{ MeV}$) via its progeny, ^{90}Y ($\beta_{\text{max}} = 2.27 \text{ MeV}$) in aqueous solutions by Cerenkov counting (see Procedure Ba-01-R; Scarpitta and Fisenne, 1996).

Cerenkov counting is applicable for β particles with maximum energies $> 0.263 \text{ MeV}$. Alpha and gamma emitting nuclides are not detected. Immediately following separation of ^{90}Y from ^{90}Sr , a baseline count rate, C_b , is obtained to quantify any Cerenkov contribution by other nuclides that may be present in the sample.

Yield recovery is determined by adding 30 mg of Sr^{+2} carrier to the sample or by gamma counting the added ^{85}Sr tracer. The sample is Cerenkov counted at any two time intervals, t_1 and t_2 , to measure the ingrowth of ^{90}Y above C_b . Strontium-90 is calculated from the ingrowth of ^{90}Y . The Cerenkov counting efficiency for ^{90}Y in water is about 65-70%, whereas that of ^{90}Sr is $< 0.3\%$ for a 0-15 keV Cerenkov counting window. For a 20-min count time, the detection limit is about 6 mBq mL^{-1} (0.16 pCi mL^{-1}) or 0.35 dpm mL^{-1} with a relative standard deviation $< 3\%$.

SPECIAL APPARATUS

Packard Tri-Carb 2250-CA liquid scintillation spectrometer

SPECIAL REAGENTS

1. NIST traceable $^{90}\text{Sr}/\text{Y}$ reference standard of known activity (about 1000 dpm g^{-1}) to determine the ^{90}Y Cerenkov counting efficiency.
2. TRU Resin - Eichrom Industries, 8205 Cass Ave., Suite 107, Darien, IL 606651.

DETERMINATION

1. Dispense about 8-16 Bq of ^{90}Sr gravimetrically into either a 20 mL low ^{40}K borosilicate glass or plastic scintillation vial (see **Note 1**).
2. Add 10 mL of deionized water.
3. Prepare a blank using 10 mL of water.
4. Count both samples three times for 10-min each using the net average count rate to determine the ^{90}Y counting efficiency, $E^{90}\text{Y}$ (counts min^{-1} dpm $^{-1}$).
5. Preset the Packard Tri-Carb to Protocol 4 for Cerenkov determinations (Scarpitta and Fisenne, 1996). (**Note:** The Cerenkov counting window is typically 0-15 keV, although the full window, 0-2000 keV, may be used with a 50% increase in background.)
6. Obtain a sample containing an unknown amount of ^{90}Sr .
7. Add 30 mg of Sr^{++} carrier (as nitrate) to the sample for yield recovery.
8. Prepare an identical vial containing water as a Sr^{++} reference standard.

9. Reduce a premeasured amount, M_g (g), of sample to be tested to 10 mL to improve counting statistics.

Note :

1. A wavelength shifter, ANSA (7-Amino 1,3 Naphthalene di-Sulfonic Acid) can be used to enhance the Cerenkov counting efficiency but is not recommended if strontium yield recovery is to be determined gravimetrically. Nuclides that produce a Cerenkov signal in 25 mM ANSA are shown in Figure 1 (see Scarpitta and Fisenne, 1996).

SEPARATION

1. Separate the ^{90}Y from the ^{90}Sr by either oxalate precipitation (see Procedure Sr-03-RC) or EiChrom's TRU Spec extraction chromatographic resin. Record the separation date and time, t_0 .
2. Obtain a net baseline count rate for C_b immediately following ^{90}Y separation, using Protocol No. 4 on the Packard Tri-Carb 2250 CA counter and the Cerenkov counting window (0-15 keV).

CALCULATIONS

1. Recount the ^{90}Sr fraction three times a day over a 2-day period using the count rates (counts min^{-1}) CT_1 , CT_2 and CT_3 to calculate the ^{90}Sr activity in Step 2. The times t_1 , t_2 and t_3 are the number of hours after ^{90}Y separation in Step 1 of **Separation**.
2. Use the ^{90}Sr calculation as follows when ^{89}Sr is not present in the sample. (**Note:** A Basic computer program is provided in the Appendix to perform the ^{90}Sr calculations.)

$$A_1^{90}\text{Sr} (Bq\text{ kg}^{-1}) = \frac{(CT_2 - CT_1) - C_b}{60 \times M_S \times E^{90}\text{Y} \times [\exp\{-\lambda(t_1 - t_0)\} - \exp\{-\lambda(t_2 - t_0)\}]} \quad (1)$$

$$A_2 \text{ } ^{90}\text{Sr} \text{ (Bq kg}^{-1}\text{)} = \frac{(CT_3 - CT_1) - C_b}{60 \times M_s \times E \text{ } ^{90}\text{Y} \times [\exp\{-\lambda (t_1 - t_0)\} - \exp\{-\lambda (t_3 - t_0)\}]} \quad (2)$$

where

λ = ^{90}Y decay constant - 0.01083 h⁻¹

$E \text{ } ^{90}\text{Y}$ = ^{90}Y Cerenkov counting efficiency (counts min⁻¹ dpm⁻¹)

M_s = mass of sample (kg)

3. Obtain the average of the two ^{90}Sr activity concentrations, A_1 and A_2 from Step 2.
(**Note:** A third count could be obtained with Equation 2 if modified accordingly.)
4. Using the sample vial and the Sr^{+2} reference standard, precipitate the strontium as the carbonate, filter, dry and weigh each to obtain the yield recovery. Correct the value obtained in Step 3, dividing by the yield recovery factor. (**Note:** Gamma emitting ^{85}Sr can be added to the sample in Step 7 of **Determination** instead of Sr^{+2} .)

REFERENCES

Sanderson, C. G. and P. Greenlaw

“Semi-Annual Report of the Department of Energy, Office of Environmental Management, Quality Assessment Program”

USDOE Report EML-581, July (1996)

Scarpitta, S. C. and I. M. Fisenne

“Cerenkov Counting as a Complement to Liquid Scintillation Counting”

Appl. Radiat. Isot., 47, 795-800 (1996)

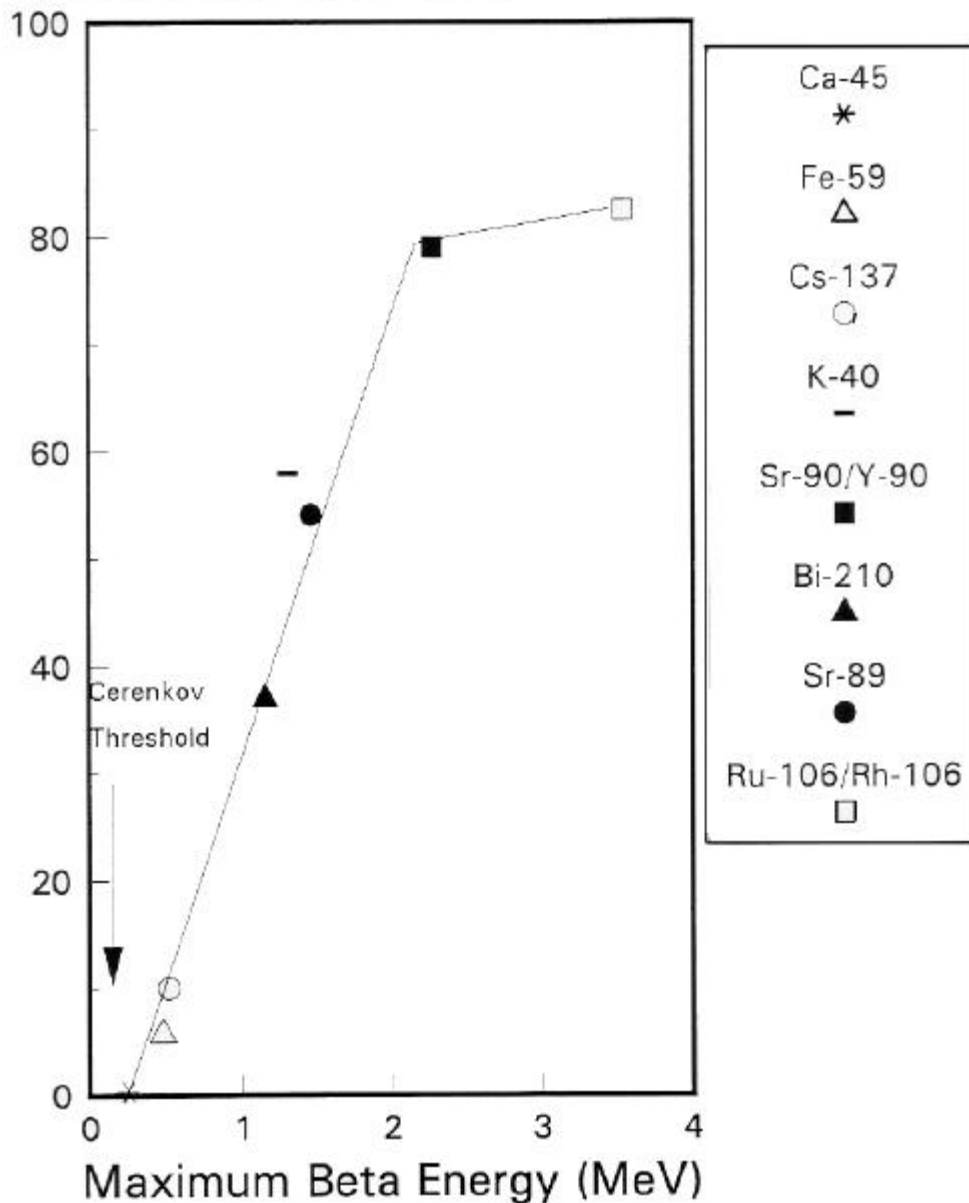
Scarpitta, S. C. and I. M. Fisenne

“Calibration of a Liquid Scintillation Counter for Alpha, Beta and Cerenkov Counting”

USDOE Report EML-583, July (1996)

Cerenkov Efficiency in 10 ml of 25 mM ANSA (Plastic Vials)

% Efficiency (0-50 keV)



ANSA = 7-Amino 1,3 Naphthalene di-Sulfonic Acid

Figure 1. Cerenkov efficiency in 10 mL of 25 mM ANSA (plastic vials).

APPENDIX

Basic Computer Program

```

10  REM "SR90CER.BAS" BY J.CHANG METHOD
20  REM CALCULATE 90SR ACTIVITY(DPM) FOR A SAMPLE USING CERENKOV COUNTING
50  TITLES--"Test of Cerenkov Method Using 895 dpm of NIST 90-Sr Standard"
60  COUNTIMES="10 min"
100 REM ENTER TIME DATA HERE
120 DELT1=.75 ' HRS
122 DELT2=19.22
124 DELT3=111.6
130 REM ENTER COUNT RATES HERE
132 CT1=36.5
134 CT2=159.1
136 CT3=514.4001
150 LAMBD2=.01083 ' HR-1
160 EFFY90=.82 ' CPM/DPM
200 REM CALCULATE SR90 ACTIVITY(DPM) HERE
205 DF1=EXP((-LAMBD2*DELT1))-EXP((-LAMBD2*DELT2))
210 A1SR90=(CT2-CT1)/(DF1*EFFY90)
255 DF2=EXP((-LAMBD2*DELT1))-EXP((-LAMBD2*DELT3))
260 A2SR90=(CT3-CT1)/(DF2*EFFY90)
500 REM PRINT RESULTS
510 CLS:SCREEN 2:KEY OFF
520 PRINT DATES;" ";
525 PRINT "STRONTIUM-90 RESULTS BY Sr-SPEC and CERENKOV COUNTING":PRINT
530 PRINT TAB(10);TITLES:PRINT
535 PRINT TAB(15);"Count Time = ";COUNTIMES;TAB(40);"Y-90 Efficiency = ";EFFY90:
    PRINT:PRINT
540 PRINT "Data":PRINT
550 PRINT TAB(1);"Del T1";TAB(10);"Cnt T1";TAB(30);"Del T2";TAB(40);"Cnt T2";TAB(60);"Del T3";TAB(70);"Cnt T3"
555 PRINT TAB(1);" (hr) ";TAB(10);" (cpm) ";TAB(30);" (hr) ";TAB(40);" (cpm) ";TAB(60);" (hr) ";TAB(70);" (cpm)":PRINT
557 PRINT TAB(1);DELT1;TAB(10);CT1;TAB(30);DELT2;TAB(40);CT2;TAB(60);DELT3;TAB(70);CT3
560 PRINT:PRINT:PRINT:PRINT "Sr-90 Results";
570 PRINT TAB(30);A1SR90;" dpm";TAB(60);A2SR90;" dpm"
575 PRINT TAB(1);"Obs/Exp";TAB(30);A1SR90/895;" ";TAB(60);A2SR90/895;
580 PRINT:PRINT:PRINT

```

02-21-1995 STRONTIUM-90 RESULTS BY Sr-SPEC and CERENKOV COUNTING

Test of. Cerenkov Method Using 895 dpm of NIST 90-Sr Standard

Count Time -- 10 min Y-90 Efficiency -- .82

Data

Del T1 (hr)	Cnt T1 (cpm)	Del T2 (hr)	Cnt T2 (cpm)	Del T3 (hr)	Cnt T3 (cpm)
.75	36.5	19.22	159.1	111.6	514.4001
Sr-90 Results		831.421 dpm		840.6198 dpm	
Obs/Exp		.928962		.9392401	

Ok

Technetium

Tc-01-RC

TECHNETIUM-99 IN WATER AND VEGETATION
(see Volume II)

Thorium

Th-01-RC

THORIUM IN URINE
(see Volume II)

Uranium

U-01-RC

ENRICHED URANIUM IN URINE
(see Volume II)

U-02-RC

**ISOTOPIC URANIUM IN BIOLOGICAL
AND ENVIRONMENTAL MATERIALS**

Contact Person(s) : Isabel M. Fisenne

APPLICATION

This procedure has been used to analyze soft tissue, vegetation, water, and air filter samples (Hindman, 1983; Sill and Williams, 1981; Welford et al., 1960).

Uranium from acid leached, dry-ashed and wet-ashed materials is equilibrated with ^{232}U tracer, and is isolated by anion exchange chromatography. The separated U isotopes are microprecipitated for α spectrometry.

SPECIAL APPARATUS

1. Ion exchange columns (see Specification 7.5).
2. Polyethylene dispensing bottles (see Specification 7.11).
3. Special apparatus for the microprecipitation of U are listed under the generic procedure, G-03.

SPECIAL REAGENTS

1. Uranium-232 tracer solution - about 0.3 Bq g^{-1} of solution in a dispensing bottle.
2. Bio Rad AG 1-X4 (100-200 mesh), anion exchange resin (see Specification 7.4).

SAMPLE PREPARATION

A. Vegetation and soft tissue.

1. Dry ash the sample according to the method described in Procedure Sr-02-RC (see **Note 1**).
2. Weigh out 10 g of ash and transfer to a 400-mL beaker.
3. Add a weighed amount of ^{232}U tracer solution (~ 0.03 Bq) from the dispensing bottle (see **Note 2**).
4. Add 200 mL of HNO_3 to the beaker and evaporate slowly to dryness.
5. Add 25 mL of HNO_3 to the beaker. Repeat the acid addition and evaporation until a white residue is obtained. (**Note:** If silicious material is present, transfer the sample to a 100 mL platinum dish or a 100 mL Teflon beaker with HNO_3 . Add 10 mL of HF to the vessel and evaporate to dryness. Repeat additions of 25 mL HNO_3 - 10 mL HF as necessary to volatilize the silica. Remove the HF by adding three successive 10-mL volumes of HNO_3 to the vessel and evaporate to dryness.)
6. Add 25 mL of HCl and evaporate to dryness. Repeat the acid addition and evaporation twice more.
7. Heat to dissolve the residue in 50-100 mL of 7N HCl.
8. Continue with **Determination**.

B. Water.

1. Evaporate the H_2O sample to a small volume.
2. Add a weighed amount of ^{232}U tracer solution (~ 0.017 Bq) from a dispensing bottle and evaporate slowly to dryness (see **Note 2**).

3. Add 50 mL of HNO_3 and evaporate to dryness. Add 25 mL of HNO_3 and evaporate twice more.
4. Dissolve the residue in 25 mL of HCl and evaporate to dryness. Repeat the HCl addition and evaporation.
5. Heat to dissolve the residue in ≤ 50 mL of 7N HCl .
6. Continue with **Determination**.

C. Air filters.

Cellulose filters:

1. Add a weighed amount of ^{232}U tracer solution (~ 0.017 Bq) from a dispensing bottle to the filter in a platinum dish and dry ash in an electric muffle at 550°C (see **Note 2**).
2. Dissolve the residue in HNO_3 and transfer to a 250-mL beaker.
3. Add 25 mL of HNO_3 and evaporate to dryness. Repeat the acid addition and evaporation twice more.
4. Dissolve the residue in 25 mL of HCl and evaporate to dryness. Repeat the HCl addition and evaporation twice more.
5. Heat and dissolve the residue in ≤ 50 mL of 7N HCl .
6. Continue with **Determination**.

Glass fiber filters:

1. Place the filter and a magnetic stirring bar in a 400-mL Teflon beaker. Add a weighed amount of ^{232}U tracer solution (~ 0.033 Bq) from a dispensing bottle.
2. Add 100 mL of HNO_3 , mechanically stir while heating for 1 h. Reduce the solution volume to ~ 25 mL. Remove the stirring bar and rinse with H_2O .

3. Add 10 mL of HF and evaporate to dryness.
4. Repeat the 25 mL HNO₃ - 10 mL HF additions and evaporations as necessary to volatilize the silica.
5. Add 25 mL of HNO₃ to the beaker and evaporate to dryness. Repeat twice more.
6. Heat and dissolve the residue in 25 mL of HCl and evaporate to dryness. Repeat the HCl addition and evaporation twice more.
7. Dissolve the residue in ≤ 50 mL of 7N HCl.
8. Continue with **Determination**.

DETERMINATION

1. Pass the 7N HCl sample solution obtained during sample preparation through a prepared anion exchange column (see **Note 3**). Discard the column effluent.
2. Wash the column with 400 mL of 7N HCl. Discard the washings.
3. Elute the uranium with 200 mL of 1N HCl, collecting the eluate in a 250-mL beaker. Discard the resin.
4. Evaporate the eluate to near dryness.
5. Destroy any residual organic material with dropwise additions of HNO₃.
6. Evaporate the solution to dryness. Dissolve the residue in a few drops of HCl.
7. Convert the solution to the chloride with three 5-mL additions of HCl.
8. Add 1-2 mL of 1N HCl, prepared with filtered water (see Procedure G-03, Microprecipitation Source Preparation for Alpha Spectrometry). Cool to room temperature.

9. Continue the analysis under Procedure G-03, Microprecipitation Source Preparation for Alpha Spectrometry.

Notes:

1. Freeze-dried or wet tissue may be wet ashed directly in HNO₃. Proceed with Step 3 of **Vegetation and Soft Tissue**.
2. It is necessary to analyze reagent blanks with each batch of samples to correct the U results.
3. 20 mL of Bio-Rad AG1-X4, prepared according to Specification 7.4 are conditioned with 500 mL of 7N HCl.

LOWER LIMIT OF DETECTION (LLD)

Uranium Isotopes

Counter Efficiency	(%)	40
Counter Background	(cps)	3.33x10 ⁻⁶ for ²³⁸ U 3.33x10 ⁻⁶ for ²³⁴ U
Yield	(%)	85
Blank	(cps)	3.33x10 ⁻⁶ for ²³⁸ U 3.33x10 ⁻⁵ for ²³⁴ U
LLD (400 min)	(mBq)	0.0002 for ²³⁸ U 0.0005 for ²³⁴ U
LLD (1000 min)	(mBq)	0.0001 for ²³⁸ U 0.0003 for ²³⁴ U
LLD (5000 min)	(mBq)	0.0005 for ²³⁸ U 0.0001 for ²³⁴ U

REFERENCES

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"Neodymium Fluoride Mounting for Alpha Spectrometric Determination of Uranium,
Plutonium and Americium"

Anal. Chem., 55, 2460-2461 (1983)

Sill, C. W. and R. L. Williams

"Preparation of Actinides for Alpha Spectrometry without Electrodeposition"

Anal. Chem., 53, 412-415 (1981)

Welford, B. A. , R. S. Morse and J. S. Alercio

"Urinary Uranium Levels in Non-Exposed Individuals"

Am. Ind. Hyg. Asso. J., 21 (1960)

U-03-RC

ISOTOPIC URANIUM IN BONE ASH

Contact Person(s) : Isabel M. Fisenne

APPLICATION

This procedure has been used to analyze 50 g human bone ash samples (Fisenne et al., 1980; Hindman, 1983; Sill and Williams, 1981).

Bone ash is dissolved in acid, and the U is equilibrated with ^{232}U tracer and isolated by solvent extraction. The purified U isotopes are microprecipitated for α spectrometry.

SPECIAL APPARATUS

1. Mechanical shaker.
2. Polyethylene dispensing bottle - see Specification 7.10.
3. Special apparatus for the microprecipitation of U are listed under the generic procedure, G-03.

SPECIAL REAGENTS

1. Uranium-232 tracer solution - about 0.1 Bq g^{-1} of solution in a dispensing bottle.
2. Alamine-336, tertiary tricaprylyl amine (Henkel Corporation, 2430 N. Huachuca Dr., Tucson, AZ 85745-1273) 3:7 in toluene. Wash twice with an equal volume of 1:1 HCl. Prepare 100 mL of acid-washed 3:7 Alamine-336 for each sample.

3. Standardized sodium hydroxide 0.1N - dissolve 4 g of NaOH in H₂O and dilute to 1 L. Standardize the solution against potassium acid phthalate.
4. Phenolphthalein indicator - dissolve 0.5 g of reagent in 100 mL of 95% ethanol.

SAMPLE PREPARATION

1. Weigh 50 g of ground, dry-ashed bone and transfer to a 400-mL beaker.
2. Add a weighed amount of ²³²U tracer (~ 0.01 Bq per sample) from the dispensing bottle. (**Note:** It is necessary to analyze reagent blanks with each batch of samples to correct the U results.)
3. Add 100 mL of HCl and heat gently on a hot plate for 10 min with occasional stirring.
4. Add 70 mL of H₂O and stir to obtain a clear solution. If insoluble material is present, filter the sample through a glass fiber filter. Wash the filter with 1:1 HCl and discard the residue.
5. Cool the solution. Transfer a 100-μL aliquot of the sample into a 150-mL beaker containing 25 mL of H₂O. Add two to three drops of 0.5% phenolphthalein indicator. Stir and titrate the solution with 0.1N NaOH to the pink endpoint. Calculate the normality of the sample solution.
6. If the normality is >5.8N in HCl, proceed directly to the extraction. If the normality is <5.8N, transfer the sample to a 250-mL graduated cylinder and record the volume. Return the sample to the beaker and add an appropriate volume of HCl to the cylinder to increase the sample acid concentration to 6N. Transfer the acid to the sample beaker and proceed with the extraction.

DETERMINATION

1. Transfer 50 mL of acid-washed Alamine-336 into each of two 500-mL separatory funnels.
2. Transfer the sample to the first separatory funnel. Wash the beaker with 1:1 HCl and add the washings to the funnel.
3. Shake the separatory funnel for 5 min. Allow the phases to separate and draw off the aqueous (lower) phase into the second separatory funnel. Retain the organic phase in the first funnel.
4. Shake the second separatory funnel for 5 min. Allow the phases to separate, draw off, and then discard the aqueous (lower) phase.
5. Combine the two organic phases in one of the separatory funnels.
6. Wash the organic phase four times for 5 min with equal volumes of 1:1 HCl. Discard the washings.
7. Strip the U from the organic phase by shaking twice for 5 min with 100-mL portions of 0.1N HCl. Combine the strip solutions in a 400-mL beaker.
8. Evaporate the solution to near dryness.
9. Destroy any residual organic material with dropwise additions of HNO_3 .
10. Evaporate the solution to dryness. Dissolve the residue in a few drops of HCl.
11. Convert the solution to the chloride with three 5-mL additions of HCl.
12. Add 1-2 mL of 1N HCl, prepared with filtered water (see Procedure G-03, Microprecipitation Source Preparation for Alpha Spectrometry). Cool to room temperature.
13. Continue the analysis under Procedure G-03, Microprecipitation Source Preparation for Alpha Spectrometry.

LOWER LIMIT OF DETECTION (LLD)

Counter Efficiency	(%)	40
Counter Background	(cps)	3.33×10^{-6} for ^{238}U 6.67×10^{-6} for ^{234}U
Yield	(%)	90
Blank	(cps)	3.33×10^{-6} for ^{238}U 3.30×10^{-5} for ^{234}U
LLD (400 min)	(mBq)	0.2 for ^{238}U 0.5 for ^{234}U
LLD (1000 min)	(mBq)	0.1 for ^{238}U for ^{234}U
LLD (5000 min)	(mBq)	0.05 for ^{238}U 0.1 for ^{234}U

REFERENCES

Fisenne, I. M., P. M. Perry, and G. A. Welford

"Determination of Uranium Isotopes in Human Bone Ash"

Anal. Chem., 52, 777-779 (1980)

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"Neodymium Fluoride Mounting for Alpha Spectrometric Determination of Uranium, Plutonium and Americium"

Anal. Chem., 55, 2460-2461 (1983)

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"Preparation of Actinides for Alpha Spectrometry without Electrodeposition"

Anal. Chem., 53, 412-415 (1981)

U-04-RC

URANIUM IN BIOLOGICAL AND ENVIRONMENTAL MATERIALS
(see Volume II)

4.5.5 Generic Procedures

G-01

ELECTRODEPOSITION OF THE ACTINIDES: MITCHELL METHOD

Contact Person(s) : Isabel M. Fisenne

APPLICATION

This method describes the preparation of separated actinide fractions for α -spectrometry measurement (Mitchell, 1960). It is applicable to any of the actinides that can be dissolved in HCl solution. The actinide fractions would be either the final elution from an ion exchange separation or the final strip from a solvent extraction separation.

SPECIAL APPARATUS

1. Electrodeposition apparatus - see Specification 7.15.
2. Electrolytic cells - see Specification 7.16.
3. Platinum - iridium stirrer - see Specification 7.15.
4. Virgin platinum discs - 17.6 mm x 0.006 mm; mirrored finish on one side.
5. Ring and discs - Specification 7.2.
6. Mylar film - see Specification 7.3.

SPECIAL REAGENTS

Methyl red indicator solution 0.1% in ethanol - Fisher Chemical Co.

ELECTRODEPOSITION

1. Add 5 mL of concentrated HNO_3 to the separated actinide fraction. Evaporate the solution to dryness but do not bake.
2. Dissolve the residue in 2 mL of HCl and evaporate to near dryness. Repeat the HCl and evaporate to near dryness. Repeat the HCl addition and evaporation twice more.
3. Add 1 mL of HCl and heat the solution gently. Transfer the solution to an electrodeposition cell.
4. Rinse and police the beaker with two successive 1-mL portions of water. Add the rinsing to the cell.
5. Add one drop of methyl red indicator solution to the cell and swirl the solution to mix.
6. While swirling the solution in the cell, add 7.5N NH_4OH until the pink color just disappears.
7. Adjust the solution to a persistent pink color by dropwise additions of 2N HCl with swirling to mix. Add two drops of 2N HCl in excess.
8. Dilute the solution in the cell to 5 mL with water.
9. With the platinum anode in the chuck of the stirring motor, lower the anode to about 1 cm above the platinum disc in the electrodeposition cell. Turn on the stirring motor and adjust the speed to prevent splattering.
10. Turn on the current and adjust the flow to 1.2 A. Electrodeposit with the rotating anode for 1 h. (**Note:** At EML the electrodeposition cell is supported on a lucite pedestal which is immersed in an ice water bath to minimize evaporation of the sample solution.)
11. Add 1 mL of NH_4OH to the cell to quench the electrolyte.

12. Turn off the stirring moter. Raise the stirring motor and anode assembly, and turn off the power supply. Pour off and discard the electrolyte solution. Rinse the cell with water and discard the rinse.
13. Disassemble the cell and rinse the disc with ethyl alcohol solution. Touch the edge of the disc with a tissue to absorb the excess alcohol.
14. Place the disc on a 200 to 250°C hot plate to dry.
15. Submit the sample for alpha spectrometry measurement.

INTERFERENCES

Any element present in the separated fraction that is able to be electrodeposited will be present on the metal disc. In particular, ^{210}Pb (5.30 MeV) deposited on the disc would interfere with the yield determination of ^{232}U (5.32 MeV) or ^{243}Am (5.28 MeV) tracers used in the determination of isotopic U and ^{241}Am , respectively.

Incomplete separation of rare earth elements or incomplete wet ashing for the removal of organic materials will decrease the efficiency of the electrodeposition and may result in a thick deposit unsuitable for α -spectrometry measurement.

Samples containing more than 20 μg of U are unsuitable for measurement by α spectrometry due to the thickness of the deposit.

REFERENCE

Mitchell, R. F.

"Electrodeposition of Actinide Elements at Tracer Concentrations"
Anal. Chem., 32, 326-328 (1960)

G-02

ELECTRODEPOSITION OF THE ACTINIDES: TALVITIE METHOD

Contact Person(s) : Isabel M. Fisenne and Pamela M. Perry

APPLICATION

This method describes the preparation of separated actinide fractions α -spectrometry measurement (Talvitie, 1972). It is applicable to any of the actinides that can be dissolved in dilute ammonium sulfate solution. Examples of applicable actinide fractions would be the final elution from an ion exchange separation or the final strip from a solvent extraction separation.

SPECIAL APPARATUS

1. Electrodeposition apparatus - see Specification 7.15.
2. Electrolytic cells - see Specification 7.16.
3. Platinum - iridium stirrer - see Specification 7.15.
4. Virgin platinum discs - 17.6 mm x 0.006 mm; mirrored finish on one side.

SPECIAL REAGENTS

Thymol blue indicator, sodium salt solution (0.04%) - dissolve 0.04 g of the salt in 100 mL of H₂O.

ELECTRODEPOSITION

1. Add 2 mL of 0.36M NaHSO₄ to the separated actinide fraction. Add 5 mL of concentrated HNO₃, swirl to mix, and evaporate the solution to dryness but do not bake.
2. Dissolve the residue in 5 mL of electrolyte solution and warm the solution.
3. Transfer the sample solution to the electrodeposition cell. Rinse the beaker with 5 to 10 mL of electrolyte solution and add the rinsing to the electrodeposition cell.
4. Add three to four drops of thymol blue indicator to the sample and adjust the pH with 1.8M H₂SO₄ or concentrated NH₄OH, or both, until a salmon pink color persists.
5. With the platinum anode in the chuck of the stirring motor, lower the anode to about 1 cm above the stainless steel disc in the electrodeposition cell. Turn on the stirring motor and adjust the speed to prevent spattering.
6. Turn on the current and adjust the flow to 1.2 A. Electrodeposit with the rotating anode for 1 hour. (**Note:** At EML the electrodeposition cell is supported on a lucite pedestal which is immersed in an ice water bath to minimize evaporation of the sample solution.)
7. After 1 h, add 1 mL of NH₄OH to the cell to quench the electrolyte.
8. Turn off the stirring motor. Raise the stirring motor and anode assembly and turn off the power supply. Pour off and discard the electrolyte solution. Rinse the cell with three successive portions of 0.15M HN₄OH. Discard the rinsings.
9. Disassemble the cell and rinse the disc with ethyl alcohol. Touch the edge of the disc with a tissue to absorb the excess alcohol.
10. Place the disc on a 200 to 250°C hot plate to dry.
11. Submit the sample for α -spectrometry measurement.

INTERFERENCES

1. Any element present in the separated fraction that is able to be electrodeposited will be present on the metal disc. In particular, ^{210}Pb (5.30 MeV) deposited on the disc would interfere with the yield determination of ^{232}U (5.32 MeV) or ^{243}Am (5.28 MeV) tracers used in the determination of isotopic U and ^{241}Am , respectively.
2. Incomplete separation of rare earth elements or incomplete wet ashing for the removal of organic material will decrease the efficiency of the electrodeposition and may result in a thick deposit unsuitable for α -spectrometry measurement.
3. Samples containing more than 20 μg of U are unsuitable for measurement by α spectrometry due to the thickness of the deposit.

REFERENCE

Talvitie, N. A.

"Electrodeposition of Actinides for Alpha Spectrometric Determination"

Anal. Chem., 44, 280-283 (1972)

G-03

MICROPRECIPITATION SOURCE PREPARATION FOR ALPHA SPECTROMETRY

Contact Person(s) : Isabel M. Fisenne

APPLICATION

Microprecipitates of Th, U, Pu, Am, and Cm, suitable for α -spectrometry measurements, are prepared by coprecipitation with Nd as the F. [Adapted from Sill and Williams (1981) and Hindman (1983).]

SPECIAL APPARATUS

1. Ultrasonic bath.
2. Millipore 47 mm diameter Pyrex glass filtration chimney, fitted glass support and metal clamp.
3. Millipore 47 mm diameter filters, 0.45 μm pore size.
4. Gelman 25 mm diameter polysulfone filtration chimney, stem support and stainless steel screen.
5. Gelman 25 mm Metrical filter, 0.1 μm pore size.
6. Eppendorf 100 μL pipette or equivalent.
7. 100 μL disposable pipette tips.

8. 10 mL plastic pipette.
9. 10 mL plastic culture tubes.
10. Pipetting bulb.
11. 50 mL plastic graduated cylinder.
12. 10 mL plastic graduated cylinder.
13. 20 L plastic carboy with spigot.
14. 2 L vacuum filtration flask.
15. 250 mL vacuum filtration flask.

Special Precautions - Due to the use of HF in the preparation of the reagents and in the precipitation procedure, rubber gloves must be worn and plasticware must be used as noted above.

SPECIAL REAGENTS

1. Filtered deionized water - filter 20 L of deionized water through 0.45 μm pore size Millipore filters. Store the filtered water in a 20-L capacity plastic carboy with a spigot (see Note 1).
2. 1N HCl - add 83 mL of concentrated HCl to 917 mL of filtered deionized water and store in a plastic bottle.
3. Neodymium carrier solution, 1000 $\mu\text{g mL}^{-1}$ (Spex Industries, Wayne, NJ), or equivalent (see Note 2).
4. Neodymium carrier solution, 0.5 mg mL^{-1} . Dilute 10 mL of the 1000 $\mu\text{g mL}^{-1}$ Nd carrier solution to 20 mL with filtered deionized water.

5. 48% HF.
6. Neodymium fluoride substrate solution - $10 \mu\text{g mL}^{-1}$ - pipette 5 mL of Nd carrier ($1000 \mu\text{g mL}^{-1}$) into a 500-mL plastic bottle. Add 460 mL of 1N HCl to the plastic bottle. Cap the bottle and shake to mix. Measure 40 mL of 48% HF in a plastic graduated cylinder. Uncap the bottle and add the HF. Recap the bottle and shake to mix thoroughly.
7. 0.58 N HF - pour 980 mL of filtered deionized water into a 1 L plastic bottle. Measure 20 mL of 48% HF in a plastic graduated cylinder. Uncap the bottle and add the HF. Recap the bottle tightly and shake to mix.
8. Ethyl alcohol, 100%.
9. Ethyl alcohol, 80% - mix 800 mL of 100% ethyl alcohol and 200 mL of filtered deionized water. Store in a 1 L plastic bottle.
10. Titanium trichloride, 20% solution (see Note 3).

Notes:

1. Deionized water may contain a sufficient quantity of solid material to adversely effect the resolution of the final filtered sample.
2. Neodymium is preferred as a carrier for the determination of thorium. Cerium compounds tend to contain variable and measurable quantities of thorium.
3. Titanium trichloride is an extremely powerful reducing agent, which should be used in a well-ventilated hood.

PRECIPITATION OF Th, Pu, Am, AND Cm

1. The separated Th, Pu, Am or Cm solution for precipitation should be in a 1-2 mL volume of 1N HCl or 1N HNO₃ solution. (The conditions for the precipitation of U

are noted separately.)

2. Transfer the solution to a 10-mL plastic culture tube. Wash the original sample vessel twice with 1-mL washes of the same concentration acid as the sample. Transfer the washings to the culture tube. Mix by gently shaking the tube.
3. Add 100 μL of the 0.5 mg mL^{-1} Nd carrier solution to the tube with an Eppendorf pipette. Gently shake the tube to mix the solution.
4. Add 10 drops (0.5 mL) of 48% HF to the tube and mix well by gentle shaking.
5. Place the tube in a cold-water ice bath for at least 30 min.
6. Insert the polysulfone filter stem in the 250-mL vacuum flask. Place the stainless steel screen on top of the fitted plastic filter stem.
7. Place a 25-mm Metrical filter on the stainless steel screen. **Caution** - place the less glossy side of the Metrical filter face up. The filters are usually shipped in the box in this manner, but the analyst should check each filter visually.
8. Wet the filter with 100% ethyl alcohol. Center the filter on the stainless steel screen support and apply a vacuum.
9. Lock the filter chimney firmly in place on the filter stem. Open the system to full vacuum.
10. Wash the filter with 100% ethyl alcohol, followed by a filtered deionized water wash.
11. Draw 5000 μL (5 mL) of Nd substrate solution into a plastic pipette.
12. Add 5 mL of the Nd substrate solution down the side of the filter chimney. Apply a vacuum to the filter for at least 15 sec.
13. Repeat Steps 11 and 12 with an additional 5000 μL of the substrate solution.

14. Place the sample to be filtered in a 150 mL beaker containing 25 mL of H_2O . Set the beaker in an ultrasonic unit containing about a 2.54 cm depth of H_2O .
15. Ultrasonicate the sample tube for about 1 min to suspend the NdF_3 precipitate.
16. Pour the sample down the side of the filter chimney and apply a vacuum.
17. Add about 2 mL of 0.58N HF to the tube and ultrasonicate briefly. Pour the wash down the side of the filter chimney.
18. Repeat Step 17.
19. Add about 2 mL of filtered deionized water to the tube and ultrasonicate briefly. Pour the wash down the side of the filter chimney.
20. Repeat Step 19.
21. Add about 2 mL of 80% ethyl alcohol to the tube and ultrasonicate briefly. Pour the wash down the side of the filter chimney.
22. Repeat Step 21.
23. Wash any drops remaining on the sides of the chimney down toward the filter with 80% ethyl alcohol. **Caution** - Directing of a stream of liquid onto the filter will disturb the distribution of the precipitate on the filter and render the sample unsuitable for α -spectrometry resolution.
24. Without turning off the vacuum, remove the filter chimney.
25. Reduce or turn off the vacuum to remove the filter. Discard the filtrate. (**Caution** - If the filtrate is to be retained, it should be placed in a plastic container to avoid dissolution of the glass vessel by dilute HF.)
26. Place the filter directly on a suitable mounting disc. Secure with a mounting ring.

27. Place the mounted sample under a heat lamp (sample to lamp distance should be about 10 cm) for 10 min prior to α -spectrometry measurement.

PRECIPITATION OF U

1. The U bearing solution must be in HCl solution.
2. Transfer 1-2 mL of the U bearing solution (1N HCl) to a 10-mL plastic culture tube. Wash the original sample vessel twice with 1-mL portions of 1N HCl. Transfer the washings to the culture tube. Mix by gently shaking the tube.
3. Add 100 μ L of the 0.5 mg mL⁻¹ Nd carrier with an Eppendorf pipette. Gently shake the tube to mix the solution.
4. Add four drops of 20% Ti trichloride to the tube and gently shake the tube. A strong permanent violet color should appear. If the color fails to appear, add a few more drops of Ti trichloride.
5. Continue the precipitation from Step 4, Precipitation of Th, Pu, Am, and Cm.

REFERENCES

Hindman, F. D.

"Neodymium Fluoride Mounting for Alpha Spectrometric Determination of Uranium, Plutonium, and Americium"
Anal. Chem., 55, 2460-2461 (1983)

Sill, C. W. and R. L. Williams

"Preparation of Actinides for Alpha Spectrometry Without Electrodeposition"
Anal. Chem., 53, 421-415 (1981)

4.5.6 Sequential Analyses

Se-01
ISOTOPIC URANIUM AND RADIUM-226

Contact Person(s) : Isabel M. Fisenne

APPLICATION

This procedure is applicable to 5 g soil samples, 10 g vegetation and fecal ash samples and ion exchange resin from sampling columns. [Adapted from Fisenne et al. (1980), Hindman (1983), Sill (1961), and Sill and Williams (1981).]

Tracers and carriers are added to the sample which is pretreated with HNO_3 -HF, fused with KF, and transposed to pyrosulfate. The cake is dissolved in HCl. Radium/barium sulfate is precipitated, filtered, and dissolved in alkaline EDTA. The chemical yield for Ra is determined with the γ -emitting tracer ^{133}Ba . Radium-226 is determined by ^{222}Rn emanation.

Uranium is isolated by solvent extraction. The U isotopes are coprecipitated with Nd as the F for measurement by α spectrometry.

SPECIAL APPARATUS

1. 100-mL platinum dishes or 250-mL platinum crucibles.
2. Millipore glass filtration chimney, fritted glass support, and metal clamp - 47 mm diameter.
3. Millipore filters - 47 mm diameter, 0.45 μm pore size.
4. Polyethylene dispensing bottle or similar - see Specification 7-11.

5. Mechanical shaker.
6. Special apparatus for the microprecipitation of U are listed under the generic procedure, G-03.

SPECIAL REAGENTS

1. ^{133}Ba tracer solution - about 50 cps per 0.1 g aliquot, prepared in 1:99 HCl.
2. Barium carrier solution (20 mg mL^{-1}) - 30.4 g $\text{BaCl}_2 \text{ L}^{-1}$ in 1:99 HCl.
3. EDTA solution - 300 g tetrasodium salt of EDTA L^{-1} in H_2O .
4. Triethanolamine - 1:1 in H_2O .
5. ^{232}U tracer solution - about 0.17 Bq g^{-1} of solution in a dispensing bottle.
6. Alamine-336, tertiary tricaprylyl amine (Henkel Company, 2430 N. Huachuca Dr., Tucson, AZ 85745-1273) 3:7 in toluene. Wash twice with an equal volume of 1:1 HCl. Prepare 100 mL of acid-washed 3:7 Alamine-336 for each sample.

SAMPLE PREPARATION

A. Soil and vegetation.

1. Weigh 5 g of soil or 10 g of fecal or vegetation ash into a 100-mL platinum dish. Add a weighed aliquot (about 0.1 g) of ^{133}Ba tracer solution and 1 mL of Ba carrier solution. Add a weighed aliquot of ^{232}U tracer solution (about 1 g for soil and about 0.5 g for fecal or vegetation ash).
2. Slowly add 10 mL of HNO_3 and 10 mL of HF to the sample and evaporate on a hot plate to near dryness.
3. Continue the analysis as described under **Determination**.

B. Ion exchange resin.

1. Transfer the resin and paper pulp from the collection column (see Specification 7.4) to a 250-mL platinum crucible. Dry under a heat lamp and ash at 500°C in a muffle furnace for 48 h.
2. To the cooled crucible, add a weighed aliquot (about 0.1 g) of ^{133}Ba tracer solution and 1 mL of Ba carrier solution. Add a weighed aliquot (about 0.1 g) of ^{232}U tracer solution.
3. Continue the analysis as described under **Determination**.

DETERMINATION

A. Radium separation.

1. Weigh out 15 g of KF and add to the sample. Press the KF into the sample with a plastic spatula.

Caution: Wear rubber gloves and safety glasses during Steps 2-5.

2. Fuse the sample over an air-fed Meker burner, gradually increasing the temperature until a clear melt is obtained. Cool the melt.
3. Using a burette, slowly add 17.5 mL of H_2SO_4 to the melt. Heat the dish on a hot plate until the cake dissolves and evaporate until SO_3 fumes appear.
4. Weigh out 10 g of Na_2SO_4 , add to the dish and fuse over a blast burner until a clear melt accompanied by dense fumes is obtained. Cool the melt.
5. Transfer the cake to a 600-mL beaker containing 350 mL of hot water and 25 mL of HCl. Stir the solution to dissolve the cake. Cool for 1 h.

6. Filter the precipitate onto a 47 mm diameter 0.45 μm pore size Millipore filter, police the beaker and wash with H_2O . Reserve the filtrate for U separation.
7. Using a strong stream of H_2O from a wash bottle, transfer the precipitate to a 150-mL beaker. Discard the filter.
8. Add 5 mL of EDTA solution and 1 mL of 1:1 triethanolamine to the beaker. Heat on a warm hot plate for about 15 min, adding 10 mL of H_2O and stirring occasionally. Reduce the sample volume to about 15 mL.
9. Filter the warm solution by gravity through a Whatman No. 42 filter paper into a 30-mL polyethylene bottle.
10. Wash the beaker and filter with hot water. Discard the filter.
11. Dilute the sample to the same liquid level as a known aliquot (about 0.1 g) of the ^{133}Ba tracer solution diluted to 25 mL in a 30-mL polyethylene bottle.
12. Gamma count the samples and standard to determine the chemical yield of Ba.
13. Transfer the sample to a ^{222}Rn bubbler with H_2O .
14. De-emanate ^{222}Rn by bubbling with forming gas for about 10 min at 100 mL min^{-1} as described in the Emanation Procedure for ^{226}Ra , Ra-03. Record the time as the starting time for ^{222}Rn buildup. Continue the analysis by the emanation technique.

B. Uranium separation.

1. Evaporate the reserved filtrate (**Radium Separation**, Step 6) to a 150-mL volume.
2. Add 150 mL of HCl to the sample solution and stir.
3. Remove the sample from the hot plate and cool to room temperature.
4. Transfer 100 mL of acid washed Alamine-336 into a 500-mL separatory funnel.

5. Transfer the sample solution into the separatory funnel. Wash the beaker with 1:1 HCl and add the washings to the funnel.
6. Shake the separatory funnel for 5 min. Allow the phases to separate. Draw off the aqueous (lower) phase and discard.
7. Wash the organic phase four times for 5 min with equal volumes of 1:1 HCl. Discard the washings.
8. Strip the U from the organic phase by shaking twice for 5 min with 100-mL portions of 0.1N HCl. Combine the strip solutions in a 400-mL beaker. Place the organic phase in a suitable container for disposal.
9. Evaporate the strip solution to near dryness.
10. Destroy any residual organic material with dropwise additions of HNO₃.
11. Evaporate the solution to dryness. Dissolve the residue in a few drops of HNO₃.
12. Convert the solution to the chloride with three 5-mL additions of HCl.
13. Add 1-2 mL of 1N HCl, prepared with filtered water (see Procedure G-03, Microprecipitation Source Preparation for Alpha Spectrometry).
14. Continue the analysis under Procedure G-03, Microprecipitation Source Preparation for Alpha Spectrometry.

LOWER LIMIT OF DETECTION (LLD)*

²²⁶Ra

Counter Efficiency	(2%)	57.5
Counter Background	(cps)	0.0028
Yield	(%)	90
Blank	(cps)	0.0020
LLD (400 min)	(mBq)	3.3
LLD (1000 min)	(mBq)	1.7

Uranium Isotopes

Counter Efficiency	(%)	40
Counter Background	(cps)	3.33x10 ⁻⁶ for ²³⁸ U 3.33x10 ⁻⁶ for ²³⁴ U
Yield	(%)	85
Blank	(cps)	3.33x10 ⁻⁶ for ²³⁸ U 3.00x10 ⁻⁵ for ²³⁴ U
LLD (400 min)	(mBq)	0.3 for ²³⁸ U 0.8 for ²³⁴ U
LLD (1000 min)	(mBq)	0.2 for ²³⁸ U 0.5 for ²³⁴ U
(5000 min)	(mBq)	0.1 for ²³⁸ U 0.2 for ²³⁴ U

*It is necessary to analyze the reagents used with each batch of samples so that blank corrections can be made for U and ²²⁶Ra.

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Fisenne, I. M., P. M. Perry, and G. A. Welford

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Anal. Chem., 53, 412-415 (1981)

Se-02
ISOTOPIC URANIUM, ISOTOPIC THORIUM AND RADIUM-226

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APPLICATION

The method is applicable to 5 g soil samples, 20 g vegetation ash samples and 50 g bone ash samples.

Soil, vegetation ash and bone ash samples are spiked with ^{229}Th , ^{232}U and ^{133}Ba tracer solutions. The soil and vegetation ash samples are pretreated with HNO_3 -HF fused with potassium fluoride and transposed to pyrosulfate. The cake is dissolved in HCl. Bone ash samples are dissolved directly in HCl. Uranium isotopes are isolated by solvent extraction and are coprecipitated with neodymium as the fluoride for alpha spectrometry measurement. Thorium is coprecipitated with calcium as the acidic oxalate. The thorium is separated by solvent extraction and coprecipitated with neodymium as the fluoride for alpha spectrometry measurement. Barium carrier is added and $\text{Ra}\cdot\text{BaSO}_4$ is precipitated, filtered and dissolved in alkaline EDTA. The chemical yield is determined with the γ -emitting tracer ^{133}Ba and ^{226}Ra is determined by radon emanation.

SPECIAL APPARATUS*

1. 100-mL platinum dishes.
2. Polyethylene transfer pipettes.
3. Separatory funnels - 125, 250, 500 and 1000 mL.

* *Special apparatus and special reagents for the microprecipitation of uranium and thorium with neodymium as the fluoride are listed in Microprecipitation of the Actinides, G-03.*

4. Wrist action separatory funnel shaker unit.
5. Millipore filtration unit - 47 mm diameter Pyrex glass filtration chimney, fritted glass support and metal clamp.
6. Millipore filters - 47 mm diameter, 0.45 μm pore size.
7. Radon bubblers - see Specification 7.7.

SPECIAL REAGENTS

1. Uranium-232 tracer solution - about 0.2 Bq g^{-1} of solution in a polyethylene transfer pipette (see **Note 1**).
2. Thorium-229 tracer solution - about 0.2 Bq g^{-1} of solution in a polyethylene transfer pipette.
3. Barium-133 tracer solution - about 10 kBq g^{-1} of solution in a polyethylene transfer pipette. Add 0.1 g of tracer to each sample.
4. Alamine-336, tertiary tricapryl amine (Henkel Corp., 2430 N. Huachuca Dr., Tucson, AZ 85745-1273) 3:7 in toluene. Wash twice with an equal volume of 1:1 HCl. Prepare 100 mL of acid-washed 3:7 Alamine-336 for each sample.
5. Aliquat-336, methyltricapryl-ammonium chloride (Henkel Corp., 2430 N. Huachuca Dr., Tucson, AZ 85745-1273) 4:6 in toluene. Wash four times with an equal volume of 2N HNO_3 and once with an equal volume of 1:1 HNO_3 . Prepare 50 mL of acid-washed 4:6 Aliquat-336 for each soil and vegetation ash sample and 100 mL for each bone ash sample.
6. Calcium propionate ($(\text{CH}_3\text{CH}_2\text{COO})_2\text{Ca}$) - solid (see **Note 2**).
7. Oxalic acid (CHO_2COOH) - solid (see **Note 2**).
8. Barium carrier solution (20 mg Ba mL^{-1}) - 30.4 g of BaCl_2 L^{-1} of 1:99 HCl.

9. Ammonium sulfate solution (100 mg mL^{-1}) - 100 g of $(\text{NH}_4)_2\text{SO}_4 \text{ L}^{-1}$ of H_2O .
10. EDTA solution - 500 g tetrasodium salt of EDTA L^{-1} of H_2O .
11. Triethanolamine - 1:1 with H_2O .

SAMPLE PREPARATION

A. Soil, milk, and vegetation ash.

1. Weigh 5 g of soil or up to 20 g of milk or vegetation ash into a 100-mL platinum dish. Add weighed aliquots of ^{133}Ba , ^{229}Th and ^{232}U tracer solutions (see **Note 3**).
2. Slowly add 10 mL of HNO_3 and 10 mL of HF to the sample and evaporate on a hot plate to near dryness.
3. Continue the analysis as described under **Sample Dissolution**.

B. Bone ash.

1. Weigh 50 g of ground, dry ashed bone into a 400-mL beaker. Add weighed aliquots of ^{133}Ba , ^{229}Th and ^{232}U tracer solutions (see **Note 3**).
2. Continue the analysis as described under **Sample Dissolution**.

SAMPLE DISSOLUTION*

A. Soil, milk, and vegetation ash.

1. Weigh 15 g of KF and sprinkle over the surface of the sample.

* Based upon Sill (1981).

2. Fuse the sample over a Meker burner, gradually increasing the temperature until a clear melt is obtained. Cool the melt.
3. Slowly add 17.5 mL of H_2SO_4 to the melt. Heat the dish on a high temperature hot plate until the cake dissolves and heat until sulfur trioxide fumes appear.
4. Weigh 10 g of Na_2SO_4 , add to the dish and fuse over the Meker burner until a clear melt, accompanied by dense fumes, is obtained. Cool the melt.
5. Transfer the cake to a 600-mL beaker containing 250 mL of hot 1:1 HCl. Stir the solution to dissolve the cake. If necessary, add additional HCl to completely dissolve the cake. Cool for 1 h.
6. Continue the analysis as described under **Uranium Separation**.

B. Bone ash.

1. Add 100 mL of HCl and heat gently on a hot plate for 10 min with occasional stirring.
2. Add 70 mL of water and stir to obtain a clear solution. Cool the solution for 1 h.
3. Continue the analysis as described under **Uranium Separation**.

URANIUM SEPARATION*

1. Transfer 50 mL of acid-washed Alamine-336 into each of two 500-mL separatory funnels.
2. Transfer the sample to the first separatory funnel. Wash the beaker with 1:1 HCl and add the washings to the funnel.

*Based on Fisenne et al. (1980)

3. Shake the separatory funnel for 5 min. Allow the phases to separate and draw off the aqueous (lower) phase into the second separatory funnel. Retain the organic phase in the first funnel.
4. Shake the second separatory funnel for 5 min. Allow the phases to separate, draw off the aqueous phase into a 2000-mL beaker for subsequent analyses of thorium and radium.
5. Combine the two organic phases in one of the separatory funnels.
6. Wash the organic phase four times for 5 min with an equal volumes of 1:1 HCl. Combine the washings in the 2000-mL beaker (Step 4).
7. Strip the uranium from the organic phase by shaking twice for 5 min with 100-mL portions of 0.1N HCl. Combine the strip solutions in a 400-mL beaker. The organic phase is placed and retrained in a suitable disposal container (see **Note 4**).
8. Add 1 mL of H₂SO₄ to the strip solution and evaporate the solution to sulfur trioxide fumes.
9. Destroy any residual organic material with dropwise additions of HNO₃.
10. Evaporate the solution to dryness. Dissolve the residue in a few drops of HCl.
11. Convert the solution to the chloride with three 5-mL additions of HCl.
12. Add 1-2 mL of 1N HCl, prepared with filtered water (see Microprecipitation). Cool to room temperature.
13. Continue the analysis under Microprecipitation of the Actinides, G-03.

THORIUM SEPARATION*

A. Calcium oxalate collections.

1. Add 0.5 g of calcium carrier (2.5 g of calcium propionate) to the sample waste and wash solutions reserved from Steps 4 and 6 in **Uranium Separation**.

Note: DO NOT ADD CALCIUM CARRIER TO BONE ASH OR MILK SAMPLES.

2. Evaporate the solution volume to 100-200 mL.
3. Dilute the solution to 1400 mL with deionized water. Heat the solution to near boiling.
4. Adjust the pH to 2.5 with NH_4OH .
5. Add 10 g of oxalic acid to soil, milk, and vegetation ash samples. Add 25 g of oxalic acid to bone ash samples.
6. Stir and heat the solution to a gentle boil. Continue heating for 5 min.
7. Adjust the pH to 2.5 with NH_4OH . Gently boil the solution for 10 min.
8. Remove the sample from the hot plate, check the pH and allow the sample to stand overnight at room temperature.
9. Decant the supernate into a 3000-mL beaker and reserve for radium analysis. Reduce the volume of the decanted solution to 500 mL or less.
10. Add 100 mL of HNO_3 to the calcium oxalate precipitate and heat to destroy the oxalate. Repeat the HNO_3 addition, if necessary.
11. Convert the sample solution to the chloride with three successive additions of 50 mL of HCl .

*Based upon Fisenne and Perry (1978).

12. Repeat Steps 5-10 for soil, milk, and vegetation ash samples. Bone ash samples require four calcium oxalate collections to remove most of the phosphate ions.
13. Wet ash the oxalate precipitate with repeated additions of 50-100 mL of HNO_3 for soil and vegetation samples. Bone samples initially require 200 mL of HNO_3 .
14. Reduce the sample solution to near dryness and add 25 mL of 1:1 HNO_3 to the soil and vegetation ash samples. Add 100 mL of 1:1 HNO_3 to the bone ash sample.
15. Warm to dissolve the calcium salts. Cool the solution to room temperature.

B. Solvent extraction separation.

1. For soil and vegetation ash samples, transfer 25 mL of acid-washed Aliquat-336 into each of two 125-mL separatory funnels. For bone ash samples, add 50 mL of acid-washed Aliquat-336 into each of two 250-mL separatory funnels.
2. Transfer the sample to the first separatory funnel. Wash the beaker with 1:1 HNO_3 and add the washings to the funnel.
3. Shake the separatory funnel for 5 min. Allow the phases to separate and draw off the aqueous (lower) phase into the second separatory funnel. Retain the organic phase in the first funnel.
4. Shake the second separatory funnel for 5 min. Allow the phases to separate, draw off the aqueous phase into the beaker with the reserved radium fraction.
5. Combine the two organic phases in one of the separatory funnels.
6. Wash the combined organic phases twice for 5 min with half volumes of 1:1 HNO_3 . Add the washings to the reserved radium fraction.
7. Strip the thorium from the organic phase by shaking for 5 min with 25 mL of concentrated HCl . Allow the phases to separate and draw off the aqueous phase into the empty separatory funnel.

8. Repeat Step 7, combining the thorium bearing aqueous phases. The organic phase should be placed and retained in a suitable disposal container (see **Note 4**).
9. Add 25 mL of toluene to the separatory funnel and shake for 5 min.
10. Allow the phases to separate and draw off the aqueous phase into a 150-mL beaker. Discard the organic phase.
11. Heat the solution gently to drive off organic vapors.
12. Reduce the sample solution volume to 10 mL. Wet ash the solution with repeated 10-mL additions of HNO_3 to remove organics. **Caution** - Do not allow the solution to reach dryness.
13. Convert the solution to the chloride with three 5-mL additions of HCl. Reduce the acid volume to near dryness.
14. Add 1-2 mL of 1N HCl, prepared with filtered water (see Microprecipitation of the Actinides, G-03). Cool to room temperature.
15. Continue the analysis under Microprecipitation of the Actinides, G-03.

RADIUM SEPARATION*

1. Add 1 mL of barium carrier ($20 \text{ mg barium mL}^{-1}$) to the reserved radium fraction.
2. Reduce the sample solution to dryness and wet ash with repeated 50-100 mL additions of HNO_3 to remove organics.
3. Convert the sample to the chloride with repeated 50-100 mL additions of HCl.
4. Dilute the sample solution to 1000 mL with water. Heat and stir to dissolve the salts. Add additional water, if necessary.

*Based upon Hallden et al. (1963).

5. Adjust the solution pH to 2.5 with NH_4OH . Cool the beaker to room temperature in a water bath.
6. Add 5 mL of $(\text{NH}_4)_2\text{SO}_4$ solution ($100 \text{ mg } (\text{NH}_4)_2\text{SO}_4 \text{ mL}^{-1}$). Stir and let stand at room temperature overnight.
7. Filter the solution through 47 mm diameter, 0.45 μm pore size Millipore filter.
8. Police and wash the beaker with water. Add the washings to the filter chimney. Wash the filter with water.
9. Place the filter with the Ra.BaSO_4 in a 150-mL beaker. Discard the filtrate.
10. Add 5 mL of warm EDTA solution and 1 mL of 1:1 triethanolamine to the beaker. Heat on a warm hot plate for about 5 min. Add 10 mL of water and stir occasionally. Continue to heat for 15 min.
11. Gravity filter the warm solution through Whatman No. 42 filter paper into a 30-mL (1 oz) polyethylene bottle.
12. Wash the beaker and filter with hot water. Discard the filter paper.
13. Dilute the sample solution to the same liquid level as a known aliquot of the ^{133}Ba tracer solution diluted to 25 mL in a 30-mL (1 oz) polyethylene bottle.
14. Gamma count the samples and standard to determine the chemical yield of barium.
15. Transfer the sample to a radon bubbler with water.
16. Determine the ^{226}Ra content of the sample as described in Emanation Procedure for Radium-226, Ra-03.

Notes:

1. The ^{232}U decays to ^{228}Th and its daughters. Therefore the activity of the thorium subseries increases with time in the ^{232}U spike. Thus, a blank correction for ^{228}Th

from the added ^{232}U tracer is required, resulting in an increasing lower limit of detection (LLD) for ^{228}Th .

2. Calcium compounds and oxalic acid contain variable and measurable quantities of ^{226}Ra . Each lot of these reagents should be checked prior to use to obtain the lowest possible reagent blank value.
3. It is necessary to analyze reagent blank samples along with each batch of samples to determine the proper blank corrections.
4. The organic phase is washed twice for 5 min with an equal volume of water and placed in a suitable disposal container.

LOWER LIMIT OF DETECTION

Based upon Fisenne et al. (1987) and Harley and Fisenne (1990).

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Se-03

AMERICIUM, PLUTONIUM AND URANIUM IN WATER

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APPLICATION

This procedure describes a method for the separation and measurement of americium, plutonium and uranium in water (adapted from Eichrom Industries, Inc., Procedure ACW03, Rev. 1.5). Americium, plutonium and uranium are separated by Eichrom resins prior to measurements by alpha spectrometry. Tracers are used to monitor chemical recoveries and to correct the results to improve precision and accuracy. This is a rapid, reliable method for the measurement of actinides in water samples that is more cost-effective and efficient than traditional ion exchange, solvent extraction and precipitation techniques.

INTERFERENCES

Actinides with unresolvable alpha energies such as ^{241}Am and ^{238}Pu or ^{237}Np and ^{234}U must be chemically separated to enable measurement. This method effectively separates these isotopes.

SPECIAL APPARATUS

1. Column rack
2. Filter - 0.45 micron

SPECIAL REAGENTS

1. Ammonium hydrogen oxalate (0.1M) - dissolve 6.31 g of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and 7.11 g of $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ in 900 mL of water, filter (Whatman No. 4 suggested) and dilute to 1 L with water.
2. Ammonium hydroxide (5 wt %) - dissolve 50 g ammonium hydroxide in 950 g of water.
3. Appropriate tracers or standards.
4. Ascorbic acid.
5. Ferrous sulfamate solution (0.6M) - add 57 g of $\text{NH}_2\text{SO}_3\text{H}$ to 150 mL of water, heat to 70°C, add 7 g of iron, in small increments until dissolved, filter (Whatman No. 4 suggested), transfer to flask and dilute to 200 mL with water. Prepare fresh weekly.
6. Hydrochloric acid (0.01M HCl) - add 0.8 mL of HCl to 900 mL of water and dilute to 1 L with water.
7. Hydrochloric acid (4M HCl) - add 333 mL of HCl to 500 mL of water and dilute to 1 L with water.
8. Hydrochloric acid (5M), oxalic acid (0.05M) solution - Dissolve 6.3 g oxalic acid dihydrate in 400 mL of water. Add 417 mL HCl. Cool to room temperature and dilute to 1 L with water.
9. Hydrochloric acid (9M HCl) - add 750 mL of HCl to 100 mL of water and dilute to 1 L with water.
10. Iron powder - a fine mesh powder dissolves faster in sulfamic acid.
11. Nitric acid (2M) - sodium nitrite (0.1M solution) - add 32 mL of HNO_3 to 200 mL of water, dissolve 1.72 g of sodium nitrite in the solution and dilute to 250 mL with water. Prepare fresh daily.

12. Nitric acid solution (0.5M) - add 32 mL of HNO_3 to 900 mL of water and dilute to 1 L with water.
13. Nitric acid solution (2M) - add 127 mL of HNO_3 to 800 mL of water and dilute to 1 L with water.
14. Nitric acid solution (3M) - add 191 mL of HNO_3 to 700 mL of water and dilute to 1 L with water.
15. Nitric acid (3M) - Aluminum nitrate (1M) solution -dissolve 212 g of anhydrous aluminum nitrate in 700 mL of water, add 191 mL of HNO_3 and dilute to 1 L with water.
16. Hydrochloric acid (4M HCl) - hydrofluoric acid (0.1M) - add 333 mL of HCl and 3.6 mL HF to 500 mL of water and dilute to 1 L with water. Prepare fresh daily.
23. TRU Resin - prepacked column, 0.7 g 100-150 micron particle size resin.
24. U/TEVA Resin - prepacked column, 0.7 g 100-150 micron particle size resin.

SAMPLE PREPARATION

1. If not already prefiltered, filter the sample through a 0.45 micron filter.
2. If samples larger than 1 L are analyzed, evaporate the sample to ~1 L.
3. Aliquot 500 to 1000 mL of the filtered sample (or enough to meet the required detection limit) into an appropriate size beaker.
4. Add 5 mL of HCl per liter of sample (0.5 mL per 100 mL) to acidify each sample.
5. Add the appropriate tracers.

6. Evaporate sample to <50 mL and transfer to a 100-mL beaker. (**Note:** For some water samples, calcium sulfate formation may occur during evaporation.) Gently evaporate the sample to dryness and redissolve in approximately 5 mL of HNO_3 . Evaporate to dryness and redissolve in HNO_3 two more times, evaporate to dryness and go to **Actinide Separation Using Eichrom's Resins**.

SEPARATION

1. Dissolve each precipitate from Step 6, **Sample Preparation**, in 10 mL of 3M HNO_3 -1.0M $\text{Al}(\text{NO}_3)_3$. (**Note:** An additional 5 mL may be necessary if the volume of precipitate is large.)
2. Add 2 mL of 0.6M ferrous sulfamate to each solution. Swirl to mix. (**Note:** If the additional 5 mL was used to dissolve the sample in Step 1, add a total of 3 mL of ferrous sulfamate solution.)
3. Add 200 mg of ascorbic acid to each solution, swirling to mix. Wait for 2-3 min. (**Note:** If particles are observed to be suspended in the solution, centrifuge the sample. The supernatant will be transferred to the column in Step 5, **Uranium separation from plutonium, americium using U/TEVA resin**. The precipitates will be discarded.)

A. Uranium separation from plutonium, americium using U/TEVA resin

1. For each sample solution, place a U/TEVA Resin column in the column rack.
2. Place a beaker below each column, remove the bottom plug from each column and allow to drain.
3. Pipette 5 mL of 3M HNO_3 into each column to condition the resin and allow to drain.
4. Place a clean, labeled 50-mL beaker below each column.

5. Transfer each solution from Step 3 into the appropriate U/TEVA Resin column by pouring or by using a plastic transfer pipette and collect the eluate.
6. Add 5 mL of 3M HNO₃ to rinse to each beaker and transfer each solution into the appropriate U/TEVA Resin column and collect eluate.
7. Add 5 mL of 3M HNO₃ into each column and collect eluate.
8. Set aside the solutions collected in Steps 5, 6 and 7 for americium and plutonium separations.
9. Pipette 4 mL of 9M HCl into each column and allow to drain. Discard this rinse. (**Note:** The rinse converts the resin to the chloride system. Some neptunium may be removed here.)
10. Pipette 20 mL of 5M HCl - 0.05M oxalic acid into each column and allow it to drain. Discard eluate. (**Note:** This rinse removes neptunium and thorium from the column. The 9M HCl and 5M HCl-0.05M oxalic acid rinses also removes any residual ferrous ion that might interfere.)
11. Place a clean, labeled beaker below each column.
12. Pipette 15 mL of 0.01M HCl into each column to strip the uranium. Allow to drain.
13. Evaporate to dryness. Treat with 5 mL of HNO₃ several times to remove traces of oxalic acid. Convert to HCl.
14. Set beakers aside for Procedure G-03, **Microprecipitation Source Preparation for Alpha Spectrometry.**

B. Plutonium and americium separation using TRU resin

1. Place a TRU Resin column in the column rack for each sample dissolved.
2. Remove the bottom plug from each column and allow each column to drain.

3. Pipette 5 mL of 2M HNO_3 into each column to condition resin and allow to drain (just prior to sample loading).
4. Transfer each solution from Step 8 of **Uranium Separation** into the appropriate TRU Resin column by pouring and/or using a plastic transfer pipette.
5. Allow the load solution to drain through the column.
6. Pipette 5 mL of 2M HNO_3 into the sample beaker and transfer this rinse to the appropriate column using the same plastic pipette.
7. Allow the initial rinse solution to drain through each column.
8. Pipette 5 mL of 2M HNO_3 - 0.1M NaNO_2 directly into each column, rinsing each column reservoir while adding the 2M HNO_3 - 0.1M NaNO_2 . (**Note:** Sodium nitrite is used to oxidize Pu^{+3} to Pu^{+4} and to enhance the plutonium/ameridium separation).
9. Allow the rinse solution to drain through each column.
10. Add 5 mL of 0.5M HNO_3 to each column and allow to drain. (**Note:** 0.5M HNO_3 is used to lower the nitrate concentration prior to conversion to the chloride system.)
11. Discard the load and rinse solutions.
12. Ensure that clean, labeled beakers or vials are below each column.
13. Add 3 mL of 9M HCl to each column to convert to HCl . Collect the eluate.
14. Add 20 mL of 4M HCl to elute ameridium. Collect the eluate in the same beaker. Evaporate to dryness. Treat with 5 mL HNO_3 several times until wet-ashing of the residue is complete. Convert to HCl . Set beakers aside for Procedure G-03, **Microprecipitation Source Preparation for Alpha Spectrometry**.
15. Rinse the columns with 25 mL of 4M HCl -0.1M HF . Discard eluate.

16. Ensure the clean, labeled beakers or vials are below each column. Add 10 mL of 0.1M $\text{NH}_4\text{HC}_2\text{O}_4$ to elute plutonium from each column.
17. Evaporate to dryness. Treat with 5 mL HNO_3 several times until wet-ashing of the residue is complete. Convert to HCl. Set beakers aside for Procedure G-03,
Microprecipitation Source Preparation for Alpha Spectrometry.

PRECISION AND BIAS

1. Precision - A relative standard deviation of 4.2% at the 0.42 Bq level has been reported for uranium. A relative standard deviation of 3.2% at the 1 Bq level has been reported for plutonium.
2. Bias - Mean chemical recoveries of 95% for americium, 93% for plutonium and 86% for uranium have been reported. Since results are corrected based on spike recovery, no significant bias exists for the method.

LOWER LIMIT OF DETECTION (LLD) NATURAL URANIUM

Counter Efficiency	(%)	30
Counter Background	(cps)	3.33 x 10 ⁻⁶ for ²³⁸ U 6.67 x 10 ⁻⁶ for ²³⁴ U
Recovery :	(%)	85
LLD (400 min)	(m Bq)	0.2 for ²³⁸ U 0.3 for ²³⁴ U
LLD (1000 min)	(m Bq)	0.1 for ²³⁸ U 0.2 for ²³⁴ U
LLD (5000 min)	(m Bq)	0.06 for ²³⁸ U 0.09 for ²³⁴ U

PLUTONIUM

Counter Efficiency	(%)	30
Counter Background	(cps)	2×10^{-5}
Recovery	(%)	75
Blank	(cps)	-
LLD (400 min)	(mBq)	0.6
LLD (1000 min)	(mBq)	0.4
LLD (5000 min)	(mBq)	0.2

AMERICIUM

Counter Efficiency	(%)	30
Counter Background	(cps)	1.6×10^{-5}
Recovery	(%)	80
LLD (400 min)	(mBq)	0.5
LLD (1000 min)	(mBq)	0.3
LLD (5000 min)	(mBq)	0.1
